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NOISE STUDIES OF INDUCTIVELY COUPLED PLASMA-FOURIER
TRANSFORM SPECTROMETRY

by



SANDRO MARRA

A THESIS

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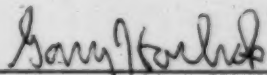
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to open the door to everlasting
wisdom but to set a limit
on everlasting error"

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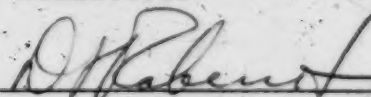
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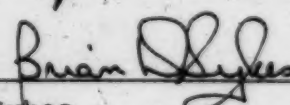
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ABSTRACT

Inductively coupled plasma-Fourier transform spectroscopy (ICP-FTS) has the potential to become an excellent combined technique for analytical atomic emission spectrometry. In particular, with a Fourier transform spectrometer the flexibility of a scanning sequential spectrometer and the speed and simultaneous measurement capability of a direct reading spectrometer can be realized at the same time. However, the noise performance and behavior of a Fourier transform spectrometer for the measurement of atomic emission spectra in the ultra-violet spectral region is not well understood or characterized. In this study the noise behavior of ICP-FTS is empirically evaluated.

The key empirical measurement carried out is the evaluation of complete standard deviation and signal-to-noise ratio spectra (i.e. those parameters measured as a function of wavenumber). A study of these spectra, along with the corresponding emission spectra as a function of concentration and matrix allows an assessment of noise distribution, multiplex advantage/disadvantage, the nature of the limiting noise, detection limits and precision. Some of the basic conclusions that can be reached from these studies are that the noise is not evenly distributed across a spectrum but is higher on and near spectral peaks, there is some distribution of noise from strong

spectral features into the baseline resulting in matrix dependent detection limits, the limiting noise at low concentrations is background photon noise, the limiting noise at high concentrations is source flicker noise and there appears to be little if any transition region of signal shot noise limiting character.

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TABLE OF CONTENTS

CHAPTER	PAGE
1. MULTIPLEX ADVANTAGE AND NOISE STUDIES.....	1
I. The Search for a Flexible and Fast Spectrometer.....	1
II. Multiplex Advantage and Disadvantage.....	3
A. Detector noise limited measurements.....	3
B. Photon shot noise and flicker noise limited measurements.....	5
1. Introduction.....	5
2. Broadband spectra.....	6
3. Narrow line spectra.....	7
4. Numerical example of the distributive multiplex gain.....	13
5. Comments and thesis objective.....	17
III. Noise Studies.....	18
A. Introduction.....	18
B. Analytical performance and noise.....	19
C. Classification and studies of noise in ICP-AES.....	26
1. Frequency composition.....	26
2. Quantitative behavior of noise with respect to the signal intensity.....	28
3. Drift and internal standardization..	30
4. Noise studies.....	32

CHAPTER	PAGE
D. Noise studies in FTS.....	33
2. EXPERIMENTAL AND STATISTICAL STUDIES.....	35
I. Introduction.....	35
II. Data Processing, Acquisition Hardware and Peripherals.....	36
III. Software.....	36
IV. Interferometer Modifications.....	39
V. Statistical Studies.....	39
A. Introduction.....	39
B. Standard Deviation and Signal-to- Noise Ratio Spectra.....	40
C. Number of Records.....	41
D. Number of Repeats for Each Run.....	45
1. What is a measurement in FTS?.....	45
2. Cadmium hollow cathode lamp statistical study.....	45
3. NOISE BEHAVIOR OF A FOURIER SPECTROMETER WITH A HOLLOW CATHODE LAMP AS A SOURCE.....	54
I. Introduction.....	54
II. Experimental Conditions and Data Presentation.....	54
III. Magnesium Hollow Cathode Lamp.....	56
A. Experimental Conditions.....	56
B. Emission, Standard Deviation and Signal- to-Noise Ratio Spectra.....	56

CHAPTER	PAGE
1. Total spectrum.....	56
2. Spectral region around the MgI 285.2 nm peak.....	59
3. Spectral region from 277 to 280 nm.....	62
4. Spectral region around the MgI 202.6 nm peak.....	65
C. Emission Spectrum.....	70
D. Comments.....	73
1. Introduction.....	73
2. Spurious spectral features.....	74
3. Spectral noise distribution.....	77
IV. Multielement Hollow Cathode Lamp.....	79
A. Experimental Conditions.....	79
B. Spectra with the Solar Blind Photo- multiplier Tube.....	79
C. Spectra with the Silicon Diode Detector and Comparison with Those Obtained with the Solar Blind Photomultiplier Tube...	87
V. Iron Hollow Cathode Lamp.....	90
A. Experimental Conditions.....	90
B. Comparison of Spectra.....	90
VI. Conclusions.....	95

CHAPTER	PAGE
4. NOISE BEHAVIOR AND QUANTITATIVE PERFORMANCES OF A FOURIER SPECTROMETER WITH AN INDUCTIVELY COUPLED PLASMA - PART I. CALIBRATION CURVE AND INTERNAL STANDARD.....	97
I. Introduction.....	97
II. Experimental Conditions.....	97
III. Quantitative Study of Magnesium.....	100
A. Introduction and Experimental Conditions.....	100
B. Emission, Standard Deviation and Signal-to-Noise Ratio Spectra.....	101
C. Peak Height Calibration Curve and Noise Behavior.....	110
D. Peak Area Calibration Curve and Noise Behavior.....	119
E. Mathematical Analysis of Limiting Noise.....	121
F. Background Noise Behavior and Comp- arison to Peak Noise Behavior.....	125
G. Interferogram and Spectrum Root Mean Square Value.....	131
H. Comments.....	136
IV. Zinc Internal Standard Study.....	139
A. Introduction.....	139
B. Experimental Conditions.....	139

CHAPTER	PAGE
C. Emission, Standard Deviation and Signal-to-Noise Ratio Spectra.....	140
D. Internal Standard Technique and Correlation Coefficient.....	144
E. Signal-to-Noise Ratio Plot.....	149
V. Conclusions.....	154
5. NOISE BEHAVIOR AND QUALITATIVE PERFORMANCES OF A FOURIER SPECTROMETER WITH AN INDUCTIVELY COUPLED PLASMA AS A SOURCE - PART II. EFFECT OF ADDING TO THE SOUGHT-FOR ELEMENT VARIOUS AMOUNTS OF A SECOND ELEMENT.....	157
I. Introduction.....	157
II. Experimental Conditions.....	158
III. Emission, Standard Deviation and Signal-to-Noise Ratio Spectra.....	158
IV. Noise Behavior of the Added Element.....	166
V. Noise Behavior of the Background.....	178
VI. Noise Behavior of the Sought-for-Element....	179
VII. Limit of Detection in Fourier Spectroscopy..	185
VIII. Conclusions.....	189
6. SUMMARY AND FUTURE RESEARCH DIRECTIONS.....	191

BIBLIOGRAPHY.....	194
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LIST OF TABLES

TABLE		PAGE
1	$(S.N.R.)_{FT}/(S.N.R.)_{Seq}$ at photon shot noise and flicker noise regimes.....	14
2	Hardware configuration.....	37
3	Tecmar Lab Master features.....	38
4	Plasma running conditions.....	99
5	Experimental conditions.....	102
6	Calculated slopes of plots of standard deviation values.....	130
7	Calculated slopes of plots of RMS values.....	134
8	Limits of detection of magnesium in various solutions.....	187
9	Limits of detection of magnesium and RMS values in various solutions.....	188

LIST OF FIGURES

FIGURE		PAGE
1.	Distribution of photon shot noise for emission spectra (reproduced from L. Mertz "Transformation in Optics", John Wiley and Sons, New York (1965)).....	8
2.	Plot of the ratio $(S.N.R.)_{FT}/(S.N.R.)_{Seq}$ at detector, photon shot and flicker noise limited situations for emission lines at three different intensities.....	16
3.	Graphical representation of some figures of merit in analytical chemistry.....	24
4.	Ideal plots of the signal-to-noise ratio and noise (standard deviation and relative standard deviation) versus signal for additive, transitive, and multiplicative noises.....	31
5.	Magnesium hollow cathode lamp: emission, standard deviation and signal-to-noise ratio spectra in the ultraviolet spectral region....	43
6.	Schematic representation of the modality of collection of experimental data and the statistics performed on them.....	44
7.	Emission spectra of cadmium hollow cathode lamp.....	47

FIGURE		PAGE
8.	Standard deviation spectra of cadmium hollow cathode lamp.....	48
9.	Signal-to-noise ratio spectra of cadmium hollow cathode lamp.....	49
10.	Amplitude interferograms of cadmium hollow cathode lamp.....	50
11.	Standard deviation interferograms of cadmium hollow cathode lamp.....	51
12.	Magnesium hollow cathode lamp: emission, standard deviation and signal-to-noise ratio spectra in the region around the MgI 285.2 nm peak.....	61
13.	Magnesium hollow cathode lamp: emission, standard deviation, and signal-to-noise ratio spectra in the 277 to 280 nm spectral region..	64
14.	Magnesium hollow cathode lamp: scale expanded emission spectrum in the 277 to 280 nm spectral region.....	66
15.	Magnesium hollow cathode lamp: emission, standard deviation, and signal-to-noise ratio spectra in the region around the MgI 202.6 nm peak.....	68
16.	Magnesium hollow cathode lamp: emission spectrum in the ultraviolet spectral region...	71

FIGURE		PAGE
17.	Magnesium hollow cathode lamp: scale expanded emission spectra in the ultraviolet spectral region.....	72
18.	Multielement hollow cathode lamp: emission, standard deviation and signal-to-noise ratio spectra obtained with the solar blind photomultiplier tube as the detector.....	81
19.	(a) Multielement hollow cathode lamp: emission spectrum obtained with the solar blind photomultiplier tube as the detector, part 1.....	82
	(b) Multielement hollow cathode lamp: emission spectrum obtained with the solar blind photomultiplier as the detector, part 2.....	83
	(c) Multielement hollow cathode lamp: emission spectrum obtained with the solar blind photomultiplier as the detector, part 3.....	84
	(d) Multielement hollow cathode lamp: emission spectrum obtained with the solar blind photomultiplier as the detector, part 4.....	85
20.	Multielement hollow cathode lamp: emission, standard deviation, and signal-to-noise ratio	

FIGURE

PAGE

	spectra obtained with the silicon diode as the detector.....	89
21.	Iron hollow cathode lamp: emission, standard deviation, and signal-to-noise ratio spectra in the ultraviolet spectral region. GAIN = 1×10^7	92
22.	Iron hollow cathode lamp: emission, standard deviation, and signal-to-noise ratio spectra in the ultraviolet spectral region. GAIN = 5×10^7	94
23.	Emission spectrum of a solution containing 10 ppm of magnesium in the ultraviolet spectral region.....	103
24.	Emission, standard deviation and signal-to-noise ratio spectra of a solution containing 10 ppm of magnesium in the ultraviolet spectral region.....	106
25.	Emission spectra of solutions containing 60 ppm, 6 ppm and 0.6 ppm of magnesium in the ultraviolet spectral region.....	109
26.	Plot of peak height emission intensity and peak height standard deviation as a function of the concentration of magnesium for the two major magnesium peaks.....	111

27.	(a) Standard deviation and signal-to-noise ratio spectra of solutions containing 100 ppm, 60 ppm, and 10 ppm of magnesium in the spectral region containing the MgII 279.6 nm and the MgII 280.3 nm peaks.....	115
	(b) Standard deviation and signal-to-noise ratio spectra of solutions containing 6 ppm, 1 ppm, and 0.6 ppm of magnesium in the spectral region containing the MgII 279.6 nm and the MgII 280.3 nm peaks.....	117
28.	Plot of peak area emission intensity and peak area standard deviation as a function of the magnesium concentration for the two major magnesium peaks.....	120
29.	Plot of peak area signal-to-noise ratio as a function of the concentration of magnesium for the two major magnesium peaks.....	122
30.	Plot of peak height signal-to-noise ratio as a function of the concentration of magnesium of the two major magnesium peaks.....	123
31.	Plot of baseline intensity and baseline standard deviation in two background regions as a function of the concentration of magnesium.....	126

FIGURE	PAGE
32. Plot of peak area standard deviation and baseline standard deviation as a function of magnesium concentration.....	129
33. Plot of interferogram and spectrum root mean square values as a function of the magnesium concentration.....	132
34. Emission spectrum of a solution containing 1 ppm of zinc and 10 ppm of cadmium (internal standard) in the ultraviolet spectral region..	141
35. Emission, standard deviation and signal-to-noise ratio spectra of a solution containing 1 ppm of zinc and 10 ppm of cadmium (internal standard) in the ultraviolet spectral region..	143
36. Emission spectrum of a solution containing 200 ppm of zinc and 10 ppm of cadmium (internal standard) in the ultraviolet spectral region.....	145
37. Emission, standard deviation and signal-to-noise ratio spectra of a solution containing 200 ppm of zinc and 10 ppm of cadmium (internal standard) in the ultraviolet spectral region.....	147
38. Peak height emission intensity as a function of the run number for the internal standard peak and the three major zinc peaks of a	

FIGURE

PAGE

	solution containing 200 ppm of zinc and 10 ppm of cadmium.....	150
39.	Peak height emission intensity as a function of the run number for the internal standard peak and the three major zinc peaks of a solution containing 10 ppm of zinc and 10 ppm of cadmium.....	151
40.	Plot of ZnI 213.9 nm signal-to-noise ratio as a function of the concentration of zinc with and without internal standard.....	153
41.	Emission spectrum of a solution containing 10 ppm of magnesium and 1600 ppm of iron in the ultraviolet spectral region.....	160
42.	(a) Emission spectrum of a solution containing 10 ppm of magnesium and 1600 ppm of iron in the ultraviolet spectral region, part 1.....	161
	(b) Emission spectrum of a solution containing 10 ppm of magnesium and 1600 ppm of iron in the ultraviolet spectral region, part 2.....	162
43.	Emission, standard deviation and signal-to-noise ratio spectra of a solution containing 10 ppm of magnesium and 1600 ppm of iron in the ultraviolet spectral region.....	164

FIGURE	PAGE
44. Emission spectrum of a solution containing 10 ppm of magnesium and 400 ppm of manganese in the ultraviolet spectral region.....	165
45. Partial emission spectrum of a solution containing 10 ppm of magnesium and 400 ppm of manganese in the ultraviolet spectral region...	167
46. Emission, standard deviation and signal-to-noise ratio spectra of a solution containing 10 ppm of magnesium and 400 ppm of manganese in the ultraviolet spectral region.....	179
47. Emission spectrum of a solution containing 10 ppm of magnesium and 400 ppm of zinc in the ultraviolet spectral region.....	170
48. Emission, standard deviation and signal-to-noise ratio spectra of a solution containing 10 ppm of magnesium and 400 ppm of zinc in the ultraviolet spectral region.....	172
49. Plots of peak area and standard deviation emission intensity of the two major peaks of the elements added, and baseline standard deviation as a function of the concentration of the element added.....	174
50. Double sided amplitude interferogram of a solution containing 10 ppm of magnesium.....	175
51. Double sided amplitude interferogram of a	

FIGURE		PAGE
	solution containing 10 ppm of magnesium and 100 ppm of zinc.....	176
52.	Double sided amplitude interferogram of a solution containing 10 ppm of magnesium and 100 ppm of iron.....	177
53.	Plots of peak area standard deviations of the two major peaks of the element added and baseline standard deviation as a function of the concentration of the element added.....	180
54.	Standard deviation and signal-to-noise ratio spectra of solutions containing 10 ppm of magnesium, 10 ppm of magnesium and 400 ppm of zinc, 10 ppm of magnesium and 1600 ppm of iron, and 10 ppm of magnesium and 400 ppm of manganese in the spectral area around the two major magnesium peaks.....	182
55.	Plots of peak area signal-to-noise ratio for the MgII 279.6 nm peak as a function of the element added.....	184

CHAPTER 1

MULTIPLEX ADVANTAGE AND NOISE STUDIES

I. The Search for a Flexible and Fast Spectrometer

Our research group has been involved for the last decade in the development of a Fourier transform spectrometer for atomic emission analysis. Four doctoral theses have been written on the subject [1-4]; three of them [2-4] dealing specifically with the use of an inductively coupled plasma as a source in combination with a Fourier transform spectrometer (ICP-FTS). As a result of this research effort several articles have been published [5-16].

The rationale behind the development of such a spectrometer for atomic emission analysis has been the conceptual search for a spectrometer which combines the flexibility of a scanning sequential spectrometer with the speed and simultaneous measurement capability of a direct reader or polychromator. The project is rather ambitious if we consider that flexibility can be equated to "research quality instrumentation" and speed to "routine analysis instrumentation". Descriptions of sequential and direct reading spectrometers along with the Michelson type

Fourier spectrometer are omitted here, because they can be found in the introductory chapters of the four theses referenced above [1-4].

The Fourier transform method has the following major characteristics: (1) simultaneous spectral measurement, (2) high spectral resolution, (3) wide spectral coverage, and (4) wavelength axis accuracy. All these characteristics are highly desirable in atomic emission analysis; nevertheless only one group in addition to ours is now actively involved in ICP-FTS research [17-18]. It seems therefore appropriate to ask ourselves "Why a method, such as Fourier transform spectroscopy, which offers so many advantageous characteristics for atomic spectrochemical analysis, is still at the stage of basic research and development and why has it not yet received the apparently deserved attention." This scientific disinterest has been fueled over the years by theoretical reviews predicting substandard performance in analytical precision for FTS in the UV and visible spectral regions [19-21]. This loss of analytical performance has been called the multiplex disadvantage and it refers to the decrease in precision or signal-to-noise ratio of the Fourier transform technique with respect to that attainable in the same measurement time by conventional sequential spectrometry.

It is interesting to note that it was the

appreciation of the opposite effect, a multiplex advantage (also called Fellgett's advantage), or gain in precision of the Fourier transform technique with respect to the conventional sequential spectrometer, that started the interest in modern Fourier transform spectroscopy [22,23].

The practical verification of the multiplex advantage along with the throughput (Jacquinot) advantage [24] has been obtained in the domain of spectral astronomical observations. The use of the Fourier transform method has significantly improved the quality of astronomical infrared spectra and has substantially decreased the observation time [25]. This success has subsequently reached the general market of IR spectrometry with the introduction by all major and minor instrument manufacturers of a host of FTIR instruments.

In the next section the multiplex advantage and disadvantage will be discussed in theoretical terms and a theoretical assessment of the extent of the multiplex disadvantage in emission spectroscopy will be presented.

II. Multiplex Advantage and Disadvantage

A. Detector noise limited measurements

The multiplex advantage refers to the gain in precision of the Fourier transform technique with respect to that attainable in the same measurement time by

conventional sequential scanning spectrometry. The multiplex advantage is obtained when (1) the measurement is detector noise limited, and (2) the noise is white or Gaussian. We define T as the available measurement time and M as the number of resolution elements observed, which is equal to the spectral bandwidth divided by the spectral resolution. In the case of a sequential scanning spectrometer, each resolution element will be observed during a time T/M , whereas in Fourier spectroscopy each one will be observed for the total measurement time T . The signal increases linearly with the observation time and the noise increases as the square root of the observation time. Thus the signal-to-noise ratio for a sequential spectrometer will be given by the following expression

$$(S.N.R.)_{Seq} \propto \frac{\frac{T}{M}}{(\frac{T}{M})^{1/2}} = (\frac{T}{M})^{1/2} \quad (1)$$

For the Fourier spectrometer the signal-to-noise ratio will assume the form:

$$(S.N.R.)_{FT} \propto \frac{T}{T^{1/2}} = T^{1/2} \quad (2)$$

An expression for the multiplex advantage is obtained by

dividing Equation 1 into Equation 2.

$$\frac{(S.N.R)_{FT}}{(S.N.R)_{Seq}} \propto \frac{T^{1/2}}{(\frac{T}{M})^{1/2}} = M^{1/2} \quad (3)$$

Equation 3 indicates that a major increase in precision is achievable with the Fourier method for observations at high resolution covering a broad spectral bandwidth.

B. Photon shot noise and flicker noise limited measurements

1. Introduction

Photon shot noise and flicker noise may become limiting noise factors in the ultraviolet and visible spectral regions, where photoelectric detectors, such as the photomultiplier tube, are used. In photon shot noise limited situations the noise registered at the detector increases as the square root of the signal and in flicker noise limited situations, the noise is linearly dependent on the signal intensity. In Fourier spectroscopy, as all resolution elements are simultaneously observed, the signal is normally increased by a factor of M , with respect to that observed in the same time with a sequential scanning spectrometer. Therefore signal dependent noises are bound to decrease the value of the

multiplex advantage attainable in straight detector noise limited situations.

Expressions for the multiplex advantage (or disadvantage) in photon shot noise and flicker noise limited situations will be derived in the next section. Two cases will be described: broadband and narrow line types of spectra. In both cases idealized representations of these spectra are considered. In particular, the narrow line spectra will be dealt with extensively since they typify the atomic emission spectra that we find in ICP-FTS.

2. Broadband spectra

Consider an idealized broadband spectrum in which the M resolution elements all have the same intensity. For FTS in a shot noise limited situation an additional factor of $M^{1/2}$ appears in the denominator of Equation 2. This is because of the dependence of the noise on the signal intensity. In a flicker noise limited situation the factor becomes M . Therefore, in photon shot noise limited situations, the expression for the multiplex advantage becomes:

$$\frac{(S.N.R.)_{FT}}{(S.N.R.)_{Seq}} \propto \frac{M^{1/2}}{M^{1/2}} = 1 \quad (4)$$

or a no gain, no loss situation.

In the case of a flicker noise limited situation the multiplex advantage turns into a multiplex disadvantage.

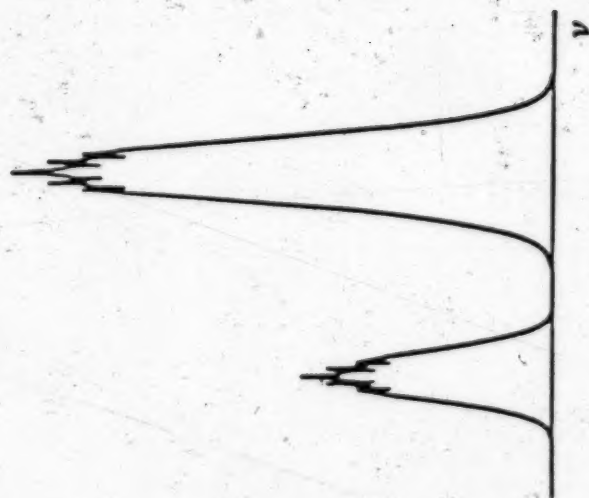
$$\frac{(S.N.R.)_{FT}}{(S.N.R.)_{Seq}} \propto \frac{M^{1/2}}{M} = M^{-1/2} \quad (5)$$

Such a measurement situation could occur when applying FTS to the measurement of molecular uv-vis absorption spectra of solution based samples.

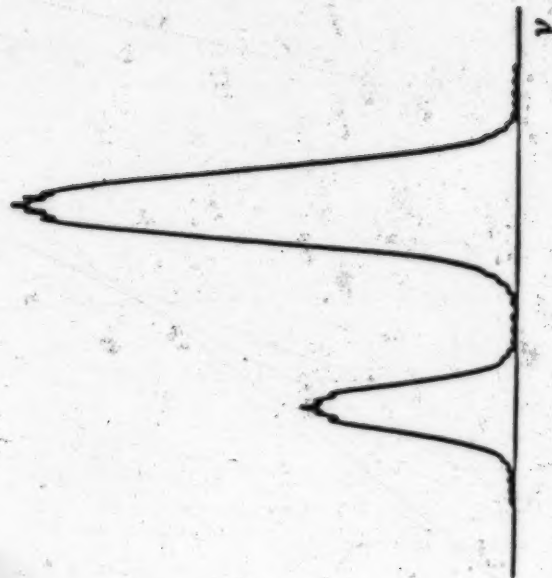
3. Narrow line spectra

An ICP atomic emission spectrum is an example of a narrow line spectrum and the measurement of such a spectrum may be photon shot noise or flicker noise limited. For these two conditions, the noise distribution over the spectrum for a sequential scanning spectrometer and a Fourier spectrometer are different. The noise distribution may be non uniform for a sequential scanning spectrometer. For instance we expect virtually no noise in the background where there is zero signal and a considerable amount of noise on the emission lines.

On the other hand in Fourier spectrometry, because of the linearity of the Fourier transformation algorithm, the noise fluctuations will be uniformly distributed over the spectrum. This different noise distribution behavior is represented schematically in Figure 1. Due to this noise distribution, a large emission line corresponding to an element present at high concentration, will lead to a decrease in precision of a low intensity line,



Sequential Spectrometer



Fourier Spectrometer

Figure 1. Distribution of photon shot noise for emission spectra (reproduced from L. Mertz "Transformation in Optics", John Wiley and Sons, New York (1965)).

corresponding to an element present at the trace level. This effect may eventually "swamp" the low intensity line and thus ultimately deteriorate the limit of detection of the element present at relatively low concentration. By the same token, the high intensity line will spread its own noise all over the spectrum which will effectively increase its own precision. It is evident, from these introductory remarks, that in the case of narrow line spectra in the uv and visible regions, we cannot talk of a uniform multiplex advantage (or disadvantage) valid throughout the spectrum. It is different for each line and it depends on the intensity of the line considered and the number and intensity of the other lines present in the spectrum. In order to derive general quantitative expressions for the multiplex advantage (or disadvantage) in atomic emission spectra the following ideal spectrum will be considered.

This spectrum is formed by M spectral resolution elements and contains a number N of narrow lines of intensity $I_1, I_2 \dots I_N$. The resolution elements with no signal ($M-N$) which form the background, have an average intensity of zero. Furthermore, for the sake of simplification, consider the M spectral resolution elements as having a width equal to one resolution element. The total time of spectral observation is T .

Accepting all these premises, we will derive the general expression for the ratio $(S.N.R.)_{FT}/(S.N.R.)_{Seq}$ for the photon shot noise and the flicker noise limited situations for any emission line with intensity I expressed in number of photons per second (the subscript n has been dropped for simplicity).

Photon shot noise limited case. In the sequential scanning spectrometer using the argument described in previous paragraphs, the signal for a line of intensity I will be proportional to $I \times T/M$ and the noise to $(I)^{1/2} \times (T/M)^{1/2}$. This results in the following signal-to-noise ratio expression

$$(S.N.R.)_{Seq} \propto (I)^{1/2} \left(\frac{T}{M}\right)^{1/2} \quad (6)$$

On the other hand in Fourier spectrometry the signal for the line of intensity I will be proportional to IT , whereas the noise will be proportional to $(I_{total})^{1/2} T^{1/2}$. I_{total} is the total intensity of the emission lines. The signal-to-noise ratio expression then has the form

$$(S.N.R.)_{FT} \propto \frac{IT}{(I_{total})^{1/2} T^{1/2}} = \frac{IT^{1/2}}{(I_{total})^{1/2}} \quad (7)$$

If we introduce a new parameter that we will call I_{average} , where $I_{\text{average}} = I_{\text{total}}/M$, we can substitute for I_{total} in Equation (7) and we obtain the following

$$(S.N.R.)_{FT} \propto \frac{I_T^{1/2}}{(I_{\text{average}} M)^{1/2}} \quad (8)$$

By ratioing Equations (8) by (6) we obtain an expression for the multiplex advantage in a photon shot noise limited situation

$$\frac{(S.N.R.)_{FT}}{(S.N.R.)_{Seq}} \propto \left(\frac{I}{I_{\text{average}}} \right)^{1/2} \quad (9)$$

The multiplex advantage in the case of a photon shot noise limited situation for line emission spectra depends upon the square root of the intensity of a line divided by the mean intensity of the whole spectrum.

Flicker noise limited case. In the sequential scanning spectrometer the signal for a line of intensity I will be proportional to $I(T/M)$. The noise, because of its direct dependence on the signal intensity will be proportional to $I(T/M)^{1/2}$. Therefore the signal-to-noise ratio expression becomes:

$$(S.N.R.)_{Seq} \propto \left(\frac{T}{M} \right)^{1/2} \quad (10)$$

In Fourier spectroscopy the signal will be proportional to I_T whereas the noise will be proportional to $I_{\text{total}} T^{1/2}$. Therefore, for the signal-to-noise ratio, the following expression is valid

$$(S.N.R.)_{FT} \propto \frac{I}{I_{\text{total}}} T^{1/2} = \frac{I T^{1/2}}{I_{\text{average}} \times M} \quad (11)$$

The ratio of (11) over (10) gives the following expression:

$$\frac{(S.N.R.)_{FT}}{(S.N.R.)_{Seq}} \propto \frac{I}{I_{\text{average}}} M^{-1/2} \quad (12)$$

Thus, in flicker noise limited situations there is a multiplex disadvantage unless the intensity of the line considered is higher than $(M)^{1/2}$ times the average intensity of the spectrum.

Equation (9) for the multiplex advantage in photon shot noise limited situations corresponds to the expression given by Kahn [26], and by Luc and Gesterkorn [27]. The flicker noise case has been discussed by Hirschfeld [28-29].

4. Numerical example of the distributive multiplex gain

In order to get some quantitative feel of the effect of lines of different intensity on the ratio $(S.N.R.)_{FT}/(S.N.R.)_{Seq}$ we will consider the following idealized spectrum. The spectrum is formed by 2048 resolution elements ($M = 2048$). It has one line of intensity $I = 1$ and one of intensity $I = 1000$. We will vary the number N of lines with intensity $I = 100$ from 1 to 1024 and we will calculate the ratio $(S.N.R.)_{FT}/(S.N.R.)_{Seq}$ by using Equations (9) and (12) for the three different lines at intensity 1, 100 and 1000. The results are tabulated in Table 1.

It is rather difficult to choose a theoretical situation which fully typifies an experimental atomic emission spectrum. Nevertheless the spectrum with $N = 16$ could be used as an example of an average atomic emission spectrum.

The photon shot noise limited situation for the line with intensity 1000 is subject to decrease in the multiplex advantage from the theoretical $\sqrt{2048} = 45$, in the detector noise limited case, to a value of 28. A further decrease of the multiplex advantage to the value of 17 is noticed for the flicker noise limited situation.

The trend is the same for the other lines at lower intensities with the worst case being the small line with

Table 1
 $(S.N.R.)_{FT}/(S.N.R.)_{Seq}$ at Photon Shot Noise and Flicker Noise Regimes

N	Photon Shot Noise			Flicker Noise		
	I=1	I=100	I=1000	I=1	I=100	I=1000
1	1.4	14	43	0.041	4.1	41
4	1.2	12	38	0.032	3.2	32
16	0.89	8.9	28	0.017	1.7	17
64	0.53	5.3	17	0.0061	0.61	6.1
256	0.28	2.8	9	0.0017	0.17	1.7
1024	0.14	1.4	4.5	0.00044	0.044	0.44

an intensity of 1 in flicker noise limited regime. A graphical representation of this drop in multiplex advantage value from the detector noise, to the photon shot noise, to the flicker noise limited situation for the three lines at different intensity ($N = 16$) is given in Figure 2.

The effect of having different values of the ratio $(S.N.R.)_{FT}/(S.N.R.)_{Seq}$ according to the intensity of the line considered and the intensity and number of lines present in the spectrum has been called distributive multiplex gain [30].

The previous theoretical treatment is based on premises which may not hold in experimental atomic emission spectra: (1) a background average value of zero, and (2) a modulation efficiency of unity. In practical atomic spectra the background may be so large as to become the limiting noise source in the measurement. In reference to the second point it should be noted that the value of the multiplex advantage of $(M)^{1/2}$ in a detector limited noise regime is subject to some debate. A more realistic $(M/8)^{1/2}$ [28,31-35] is now the accepted value. The lower value for this parameter is primarily the result of a modulation efficiency of less than unity.

Furthermore, in practice, the unmodulated signal will combine with random fluctuations to give an additional

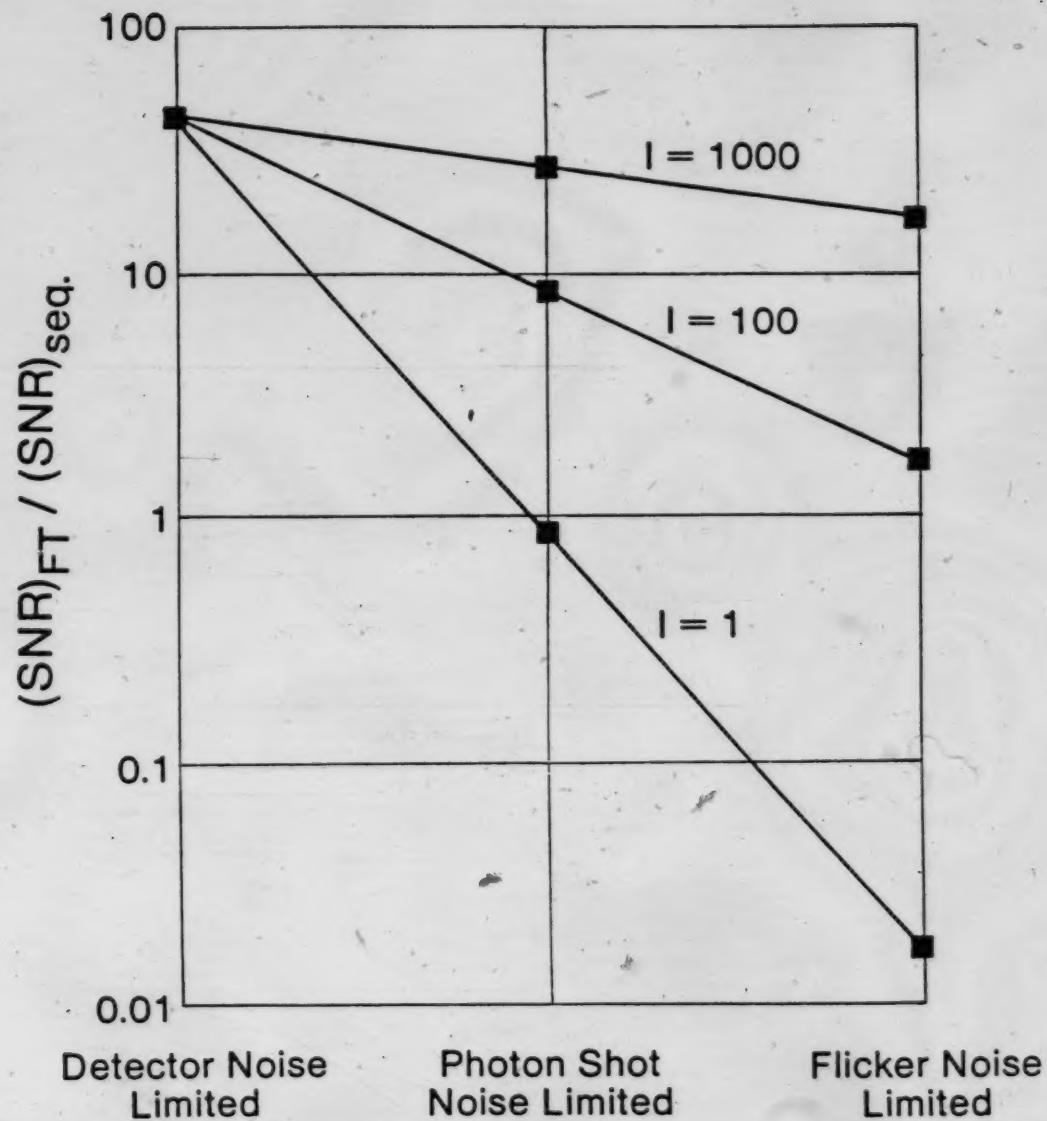


Figure 2. Plot of the ratio $(S.N.R.)_{FT} / (S.N.R.)_{Seq}$ at detector, photon shot and flicker noise limited situations for emission lines at three different intensities.

noise which will spread equally over the spectrum. More importantly systematic fluctuations such as the ones that can be observed in flicker noise regimes combined with unmodulated signal will give spurious signals (or ghosts or satellites). These, at a much lower level, are the equivalent of stray light in conventional dispersive spectroscopy.

5. Comments and thesis objective

An effect similar to the distributive multiplex gain is always present in Fourier spectroscopy, irrespectively of the noise behavior considered. It has been called the dynamic range limitation and its existence can be described in the following way. In Fourier spectroscopy we are observing all spectral features at once within the limit of the dynamic range of the analog-to-digital converter. The presence of large spectral features or large background levels may result in low intensity spectral features of less intensity than the resolution of the analog-to-digital converter. The existence of the dynamic range limitation and the distributive multiplex effect constitutes a serious impass to the general acceptance by the scientific community of the method of Fourier spectroscopy in the domain of analytical atomic emission analysis. However, previous preliminary studies in our group [2,36] and a recent communication from the

group at Los Alamos National Laboratory [37] indicates that the theoretical uniform noise distribution over the whole spectrum is not found in practice. Instead a highly peak localized noise behavior has been measured.

Briefly stated, the objectives of this thesis are:

(1) to empirically assess the magnitude of figures of merit such as signal-to-noise ratio and limit of detection for analyte lines, and (2) to study the noise distribution along the spectral axis. Both studies are vital to the understanding and assessment of the feasibility of ICP-FTS.

III. Noise Studies

A. Introduction

No detailed noise studies have been carried out to date in ICP-FTS. This section contains a review of the classification of noise and a review of the noise studies carried out on the ICP. A brief summary of noise studies in FTS will also be given. On various occasions in the course of this chapter, and in the following ones, terms relative to the noise jargon are used. Definition of terms and explanation of the figures of merit used in analytical chemistry will be given in the next section.

B. Analytical performance and noise

The analytical calibration curve, which provides the relation of the measurement of the emission intensity with the concentration of the sought-for element, sets the stage for the following figures of merit in atomic emission analysis: the sensitivity, the linear range and the limit of detection.

For a linear scale the sensitivity (m) is defined as the slope of the analytical function [38-39].

$$x = mC \quad (13)$$

where C is equal to the concentration of the element considered, m is equal to the sensitivity and x is equal to the emission intensity corresponding to the concentration C of the element considered.

A steep slope is highly desirable in analytical atomic spectroscopy. Nevertheless a high sensitivity (high slope) does not necessarily mean high analytical performance. In fact, a simple way of increasing sensitivity is to increase the amplifier gain at the instrument output. Unfortunately it will usually intensify the noise to the same extent. Sensitivities are seldom constant over large concentration ranges and are therefore meaningful only when concentration ranges are specified.

The concentration range over which the sensitivity is constant is called the linear range or the linear dynamic range and is usually expressed in number of decades between a lower and a higher limit. For inductively coupled plasma optical emission spectrometry (ICP-OES) a remarkably high, four to six decades linear range, has been reported in the literature [40-42]. The practical and theoretical implications of such an extended analytical range have been discussed in two papers [43-44].

The lower limit of the linear range is represented by what has been called the limit of detection (LOD). No other figure of merit in analytical chemistry has created more thought and stirred more scientific discussion than the limit of detection [45-58]. The main reason is that it represents conceptually the fuzzy borderline-link between the two worlds of qualitative and quantitative analysis. Moreover, nowadays many problems in analytical chemistry consist of determining (1) elements or compounds in a small amount of sample (microanalysis), (2) low concentrations or small amounts in larger samples (trace analysis), and (3) low concentrations in small samples. We may quite safely add that progress in the field of analytical chemistry can be measured by the shift of the limit of detection to lower values [50]. The accepted

IUPAC definition adopted in 1975 states that "... the limit of detection, expressed as a concentration C_L , is derived from the smallest measure x_L that can be detected with reasonable certainty for a given analytical procedure." [48]. The problem here, as it has been cleverly pictured by A.C. Menzies in the introduction to H. Kaiser "Two papers on the limit of detection of a complete analytical procedure", is "... just like searching in a stormy sea for a ship in the distance. Is the higher prominence glimpsed really a ship or a larger than usual wave?" In chemical terms the sea is the background or blank, the larger wave is a pronounced upward deviation of the background or blank and the central question "is the ship really present?" corresponds to asking ourselves "is the measurement indicating the presence of the analyte at very low concentration or is it purely background?" Statistical principles help us in trying to answer the question. Expressed in mathematical terms x_L , the smallest measure that can be detected, is equal to:

$$x_L = \bar{x}_B + kS.D.B \quad (14)$$

where $\bar{x}_B$ is equal to the mean background or blank measurement, k is equal to a constant and $S.D.B$ is equal

to the standard deviation of the background or blank measurement. C_L , the limit of detection or the concentration that corresponds to the measurement x_L , is derived by substituting Equation (14) in the analytical curve mathematical Equation (13)

$$C_L = \frac{x_L - \bar{x}_B}{m} = \frac{kS.D.B}{m} \quad (15)$$

where m is equal to the sensitivity or slope of the calibration curve. By choosing for k the value 3 and thus the allowable fluctuation of the background equal to 3 times the standard deviation of the background there is only 0.13% chance that a signal measured at x_L or greater would be a random fluctuation of the background. From the previous discussion it is apparent that the limit of detection is dependent upon the background noise. The technique "per se" in fact does not determine the magnitude of the limit of detection [60]. This figure of merit is chiefly dependent upon the analyte sensitivity and the fundamental background noise present at the detection stage.

Unlike the lower limit of the analytical calibration curve, the limit of detection, the upper limit does not have a proper name. It is regarded as the point at which the sensitivity or slope begins to change. Generally the

change is gradual and, in order to exactly define it, we have to define a certain arbitrary change in the sensitivity of the calibration curve.

A pictorial illustration of a typical calibration curve with the parameters of analytical performance discussed so far is given in Figure 3. In this figure the upper limit is considered the concentration where the response deviates 3% from the response that might have been expected from the sensitivity at lower concentrations.

Two other extremely important parameters of analytical performance are accuracy and precision. Accuracy refers to the absolute correctness of the result of "real samples" analysis and entails analysis of reference samples and/or comparison with alternative methods [61,62]. It will not be treated since the assessment of accuracy in atomic emission analysis is not an object of the present study. The concept of precision in atomic emission spectroscopy, or better, the concept of imprecision, not only has statistical significance, but is itself a statistical parameter. The standard deviation (S.D.) of the measurement of the emission intensity is the statistical representation of the imprecision of the analytical procedure.

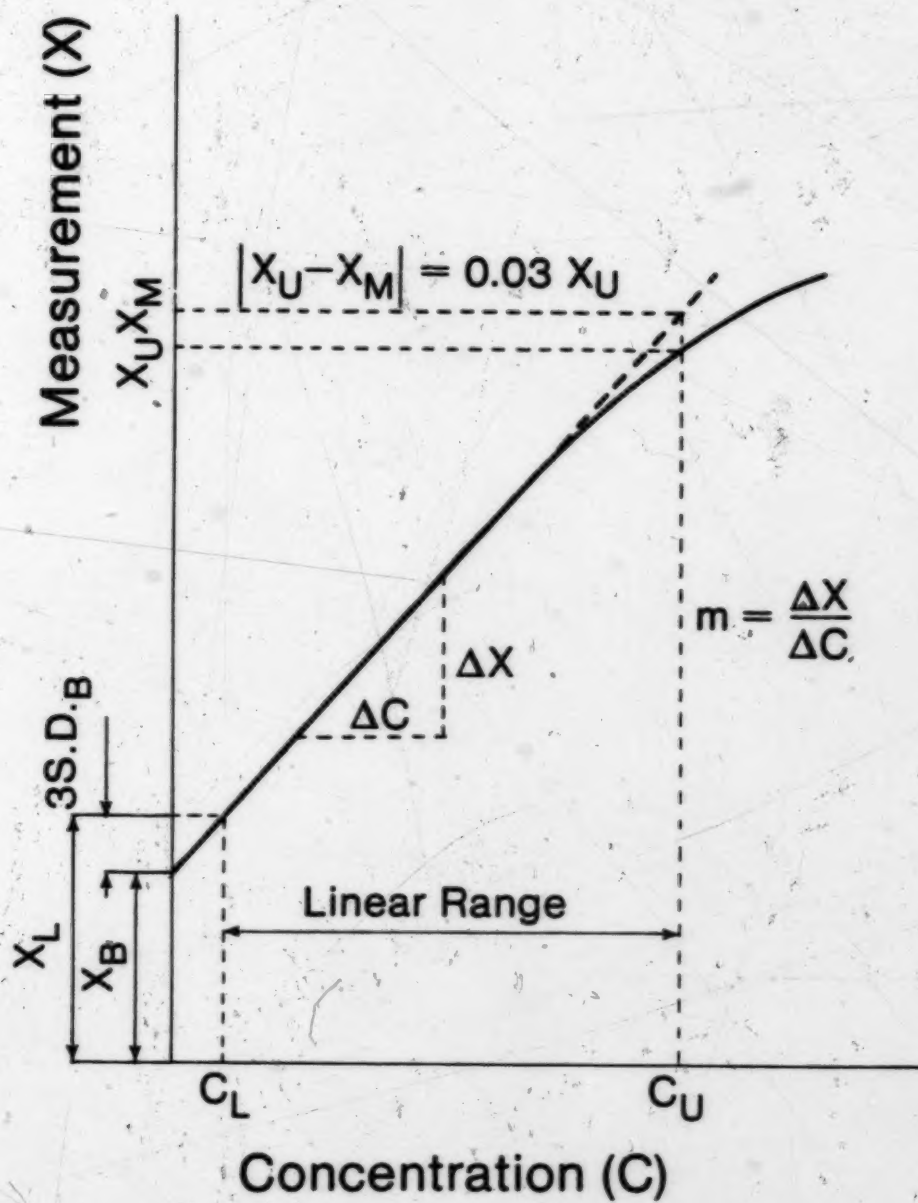


Figure 3. Graphical representation of some figures of merit in analytical chemistry.

All along the calibration curve the standard deviation of the emission intensity indicates the magnitude of the uncertainty in the result. Its value is determined by the total amount of noise present at any concentration in the calibration curve. The total noise is the sum of the individual noises present at a specified concentration. In statistical terms, since for each concentration the single standard deviations corresponding to the single independent noises add quadratically, the total noise is chiefly caused by the largest noise. This largest noise has been called the limiting noise.

Notice that in this discussion about the precision of the measurement we have not included a contribution due to non fundamental errors. Nevertheless the notion of the analytical procedure being at any time error limited instead of noise limited cannot be ruled out. The occurrence of error limited situations must be borne in mind at all times and extreme precaution must be exercised. Related to the concept of precision in the analytical procedure, a term parameter derived from the theory of signal processing, called signal-to-noise ratio (S.N.R. or S/N) is now introduced. The signal-to-noise ratio is the inverse of the relative standard deviation (R.S.D.). This parameter is particularly useful to indicate the behavior of precision with a variation of the signal level or the concentration.

C. Classification and studies of noise in ICP-AES

1. Frequency composition

Periodic noise. Periodic noise is characterized by a regular, repetitive waveform with a spectrum consisting of one or more discrete frequencies. Power line pick up, consisting mainly of the 60 Hz component, usually with some weaker harmonic components at 120 Hz, 180 Hz and so on, is an example of periodic noise. This type of noise, which has been called also interference, external, or proportional noise is obviously not fundamental in nature and, at least in principle, is easy to eliminate by placing notch filters of appropriate value at strategic points of the instrument.

Aperiodic noise. The aperiodic noise, commonly called random noise is characterized by a flat or "white" spectrum. This kind of noise is composed of virtually all the frequencies randomly placed and with randomly varying amplitudes of the individual frequency components. It is virtually impossible to totally eliminate random noise because of its, by and large, fundamental nature. Its deleterious effect on the signal can be effectively attenuated by the use of the method of signal integration [63,64] (also called signal averaging).

1/f noise (one over f noise). With respect to the frequency composition, logically located between the

aperiodic and the periodic noises, the analytical chemist is faced with a very insidious type of noise, the so-called $1/f$ noise. Its spectrum has been referred to as "pink" which means that the amplitudes of the frequencies that form the $1/f$ noise increase the closer one gets to a frequency equal to zero. Two main precautions are normally taken in ICP-AES to reduce drastically $1/f$ noise. Gas flow rates are stabilized and the analytical determination is carried out in as short a time as possible. It should be pointed out that the latter precaution strongly contrasts with the operation of signal integration which is used to correct the influence of random noise on the signal [65-69]. In actual cases the signal integration time is chosen in such a way that assures the best compromise between the opposing effect and leads to the most effective reduction of the total noise affecting the signal.

Review of noise studies. The characterization of these types of noise in ICP-AES, with respect to their frequency composition has been carried out practically through the observation of noise power spectra which are plots of noise power density versus frequency. They have been obtained in practice by Fourier transformation of the signal collected in the time domain. For details concerning the procedures for obtaining noise power spectra see references [70-74].

The noise power spectra show the presence of $1/f$ or low frequency noise [73-75] below 5 Hz and spurious 60 Hz line pick-up, in some cases with its higher harmonics [73,74,76]. A rigorous $1/f$ character is not observed in any of the studies. Maessen [75] and coworkers analyzed the disturbance and they found a character going from a $1/f^{1/2}$ to $1/f^{1/4}$ value depending on the concentration of the test element employed.

Conspicuous is the presence of high frequency acoustic noise in the 200 to 400 Hz region noticed by Winefordner and coworkers [73] and later confirmed and characterized by Belchamber and Horlick as being due to rotation in the plasma [74].

Indications of the presence of white noise are found in all the previous studies; but the universality of its frequency composition along with its effective reduction with signal averaging, renders the characterization of white noise in ICP-AES a difficult task.

2. Quantitative behavior of noise with respect to the signal intensity

Additive. To the additive types of noises belong the noises whose level is independent of the signal level. General situations where additive noise dominates the total picture are: (1) at no signal or at very low signal level when sensitive detectors, such as the photo-

multiplier tube are used, and (2) at virtually any signal level where relatively insensitive detectors, such as thermal detectors, employed in the infrared spectral region are used [77]. In this case an increase of the signal analyte concentration, say 10 fold, will correspond a 10 fold S.N.R. increase since the noise remains unchanged.

Multiplicative. Multiplicative noises are characterized by a proportionality between noise and signal levels. The already mentioned 1/f or flicker noise belongs to this category of noise. In this case an increase in signal will correspond to the same increase in noise and this will keep the S.N.R. value constant. This type of noise has been reported as being the dominating one at high signal strengths or high analyte concentration in ICP-AES.

In the central working region of a detector such as a photomultiplier tube we become what is generally referred to as photon shot noise limited. In this situation an increase in signal results in an increase in noise, although not to the same extent. The relation is quadratic, thus a 10 fold increase in signal will correspond to a $(10)^{1/2}$ fold increase in noise, which results in S.N.R. increase of $(10)^{1/2}$.

9 Photon shot noise is classified in the literature as a multiplicative type of noise. Strictly speaking, however, fluctuations caused by photon shot noise are not proportional to the signal and therefore they should not be referred to as multiplicative noise. Recently Prudnikov [78] proposed the term "transitive" or "transitional" for this kind of noise. Ideal plots of the S.N.R. and noise (signal S.D. and R.S.D.) versus the signal for the three types of noise are shown in Figure 4.

3. Drift and internal standardization

We mentioned before that in a flicker noise limited situation the noise increases exactly in the same amount that the signal does, and thus the precision remains unchanged. What is found in experimental practice at times is that the precision actually degrades [69]. It has been shown that such a behavior is caused by a noise whose frequency character is $1/f^K$ with $K > 1$ [65-66]. This would indicate that drift is, in this instance, dominating the scene. The major causes for drift are: (1) variation in sample uptake rate, (2) variation in sample nebulization efficiency as nebulizer and spray chamber change temperature, (3) variation in argon gas flow rate to the nebulizer and plasma torch, and (4) variation in sensitivity of the detector as it changes temperature. The use of internal standardization techniques has proved

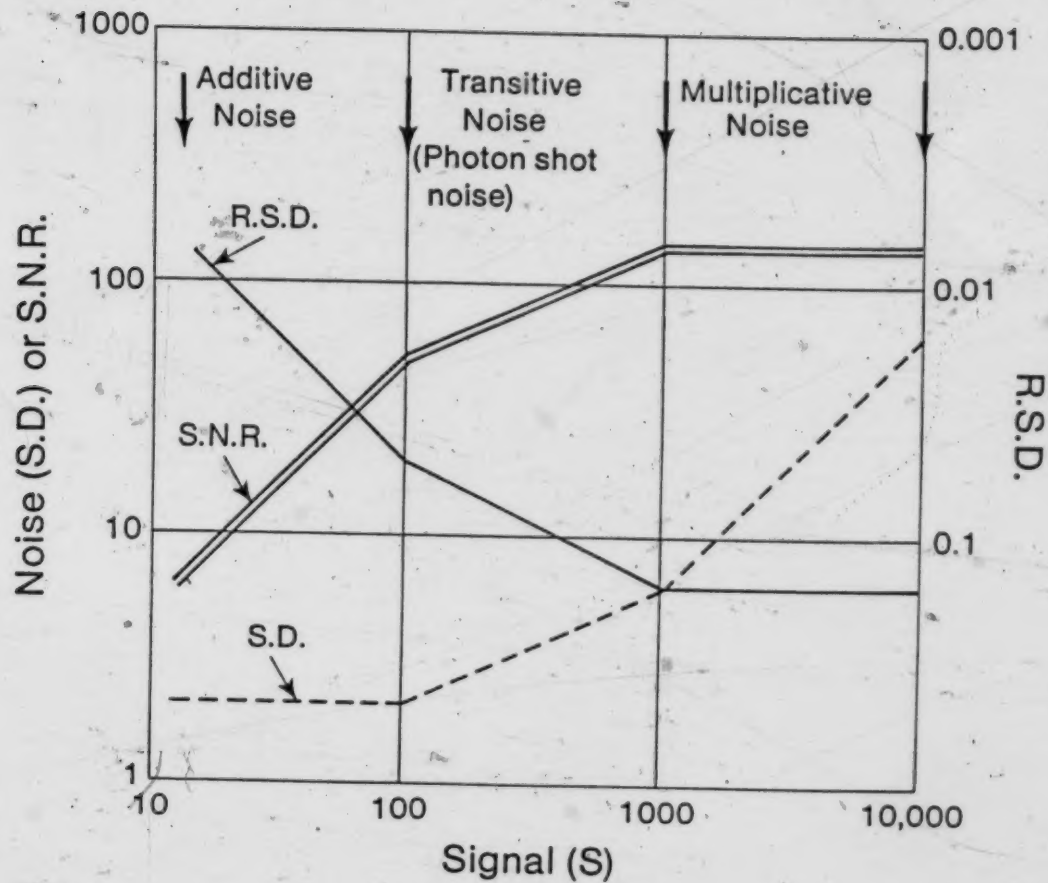


Figure 4. Ideal plots of the signal-to-noise ratio and noise (standard deviation and relative standard deviation) versus signal for additive, transitive, and multiplicative noises.

to be effective in limiting the damaging effect on analytical precision of all the multiplicative noises and errors in the ICP measurement system [79-82]. However, the possibility of becoming drift error limited at any concentration value of the analyte should always be borne in mind.

4. Noise studies

Experimental studies carried out with the ICP show that at low concentrations and in the spectral region above 250 nm, the limiting source of noise is the additive background noise [83]. Below 250 nm the plasma background is considerably reduced. Detector dark noise seems to be the dominating factor when a photodiode array is used as the detector, whereas a photon shot noise limited situation has been reported when the photomultiplier tube was used as the detector [84].

In the literature no clear definition of the extent, in terms of analyte concentration range, of the photon shot noise and, eventually of the flicker noise limited situation, is given. There are several reasons for this: (1) the ICP is considered an excellent technique for trace metal analysis, thus the large thrust of the research efforts are geared towards studies in the region very close to the analyte limits of detection, (2) overall noise studies are, generally speaking, very time

consuming, requiring several repeats for each single analyte concentration for statistical calculations, and (3) simultaneous spectral shape and contour information is not available in common ICP instrumental configurations. This kind of spectral information enables the operator to monitor the quality of the data at each step of the experimental data collection.

With reference to point (3) it should be added that ICP-FTS provides the spectral contour information. Some experimental data in this thesis will be used to characterize the noise behavior of emission from an ICP.

Finally, the interested reader should be reminded that reviews [65,67,85] and articles [65,86] containing detailed mathematical treatment of noise in atomic emission are available in the literature.

D. Noise studies in FTS

Several articles discussing multiplex advantage and signal-to-noise ratio in theoretical terms have appeared over the years [87-93]. From the theoretical standpoint undoubtedly the most authoritative discussion of noise in FTS has been written by J. Connes [93]. Her treatment is very rigorous and it describes in detail the effect of adding Gaussian noise to the signal in the time as well as in the frequency domain.

Some interesting articles dealing with sampling error effects are found in the literature [94,95].

Multiplicative noises such as scintillation and source noise on broadband spectra have been discussed in theoretical terms [29,96-97]. No practical study of the noise and error behavior in uv-vis FTS can be found in the literature.

CHAPTER 2

EXPERIMENTAL AND STATISTICAL STUDIES

I. Introduction

The modalities by which the statistical studies in ICP-FTS were carried out will be explained in detail. The major modification that made the statistical study possible was the replacement of the PDP 11/10 (Digital Equipment Corporation, DEC) as the data processing unit of the interferometer by the IBM PC/XT. Minor modifications to ensure better overall stability of the interferometer system will be described. The interferometer system has been explained and described in detail in the literature [1,2,10], therefore it will not be described in this thesis.

A block diagram and schematic of the interferometer system along with a detailed description of the mirror drive system and the control electronics used in this work are also found in the literature [4,14]. The optical coatings on the beamsplitter and mirror surfaces which made possible the successful observation of the spectral region below 240 nm are widely discussed in references 4 and 15.

II. Data Processing, Acquisition Hardware and Peripherals

The reasons for choosing the IBM PC/XT as the data processing computer for the Fourier spectrometer are several: wide availability of hardware, wide availability of software, hardware floating point capability, graphics capability, large secondary storage, possibility of future expansion, 16 bit architecture, and reasonable cost. The individual hardware components used for data acquisition, data processing and for peripherals are listed in Table 2. The main features of the Tecmar Lab Master used as the ADC interface between the Fourier spectrometer and the computer are listed in Table 3.

III. Software

The following software products were utilized: Microsoft MS-DOS 2.00, IBM Advanced Basic, IBM Assembler 1.00, Microsoft MS-Fortran 3.13, and AST printer Spooler. The data acquisition software has been written in Assembler for maximum efficiency. Also, all subroutines for graphics, a large number of utility programs and programs for interfacing to the peripherals have been written in Assembler.

The statistical programs were written in FORTRAN. The modularity and user friendliness of the software and

Table 2
Hardware Configuration

1. IBM PC/XT with:
 - Intel 8088, 4.77 MHz processor
 - 256 kbytes RAM
 - 10-megabyte fixed disk
 - 360 kbyte double-sided 5 1/4 inch floppy disk drive
2. Intel 8087 math coprocessor
3. IBM color graphics adaptor
4. IBM color IRGB monitor
5. AST Six-Pak multifunctional board with:
 - 384K RAM
 - serial interface
 - printer interface
 - joystick interface
 - real time clock
6. Tecmar Lab Master
7. Epson RX80 printer
8. Hewlett-Packard HP 7470A plotter

Table 3
Tecmar Lab Master Features

1. 12 bit ADC
 - ± 10 V DC
 - 30 kHz sampling rate
 - software, external or internal trigger
 - software programmable gain
2. Five 16 bit programmable counters
3. 24 digital I/O lines
4. Two 12 bit DAC
5. I/O or memory mapped addressing

the extensive graphics capabilities permitted strict and continuous monitoring of experimental conditions which was essential for successful statistical studies.

IV. Interferometer Modifications

An improvement on the overall interferometer signal stability and precision (about 200% better) has been obtained as a result of the following modifications:

1. the white light bulb housed in the interferometer cube was replaced by a combination white light bulb remotely located and a 1 foot connecting fiber optics cable.
2. The interferometer was enclosed in a Plexiglass case and water cooled air was forced inside the case by a fan.

V. Statistical Studies

A. Introduction

The two main goals of the work described in this thesis are:

1. To empirically assess the magnitude of statistical parameters such as standard deviation and signal-to-noise ratio of the analyte signal.
2. To study the noise distribution along the spectral-

frequency axis.

In order to achieve both goals statistical studies must be carried out.

Statistical studies in conventional spectroscopy entail the calculation of the standard deviation of a series of repetitive measurements, such as the intensity at certain given wavelengths. In the case of the polychromator, for example, the number of standard deviations that can be calculated can be, at the most, equal to the number of PMT's in the focal plane (also called channels). A typical number of channels is about 30.

In Fourier spectroscopy, due to its multiplex nature, the entire spectrum over the selected band pass is recorded at once. Therefore, in principle, there is the possibility to compute as many standard deviations as the number of spectral points in the entire spectrum. In our case the number of spectral points is 2048, since the spectra are generated by Fourier transformation of 4096 point double sided interferograms.

B. Standard Deviation and Signal-to-Noise Ratio Spectra

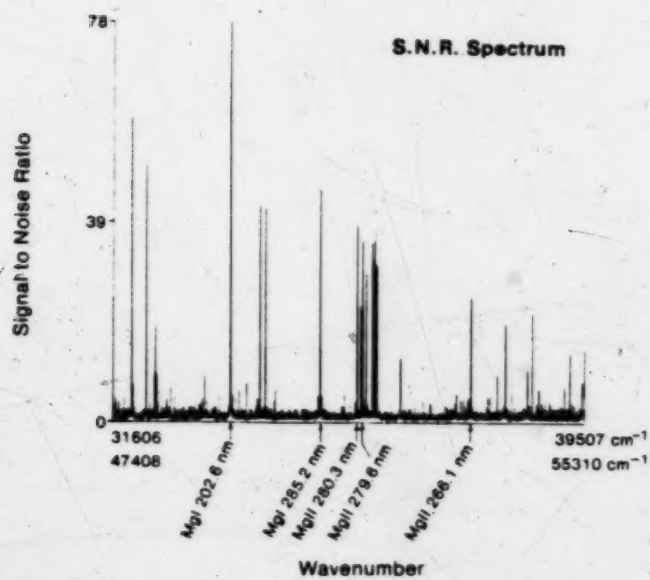
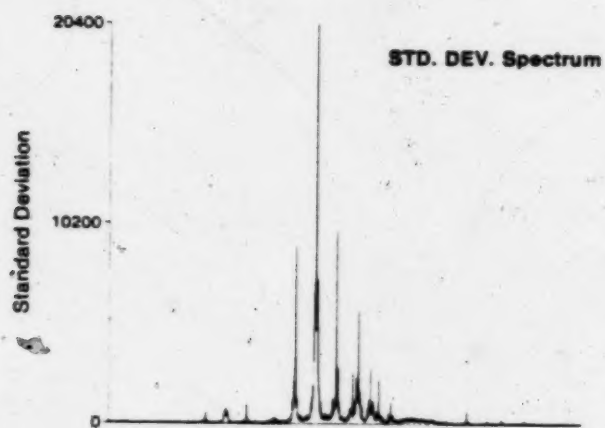
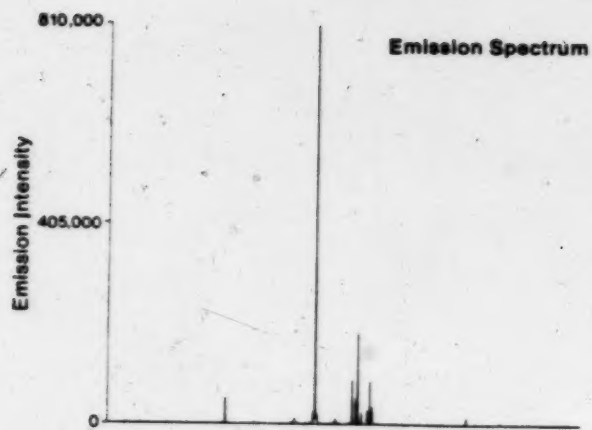
The graphical representation of these calculated standard deviations will be called a standard deviation spectrum. If the average spectrum is divided by the corresponding standard deviation spectrum a signal-to-noise ratio spectrum is the result.

An example of an experimental standard deviation spectrum, a signal-to-noise ratio spectrum and the average spectrum from which the two spectra were derived, is shown in Figure 5. The procedures used to obtain the three types of spectra, will be described in detail in the next section.

C. Number of Records

A schematic representation of the modality of collection of the experimental data and the statistical manipulations performed on them is given in Figure 6. For a datum, for example one point in a calibration curve, eight interferograms were collected and stored in a unique file. Each interferogram constitutes a record. A record will also be referred to as a run. All records were individually Fourier transformed and on the eight spectra obtained the calculation of the 2048 standard deviations were performed. The software also allowed the calculation of the 4096 standard deviations on the eight original interferogram records. Computer storage limitations dictated the maximum number (8) of records. Eight records of a 4096 point interferogram in single precision floating point format occupy about 133 kbytes.

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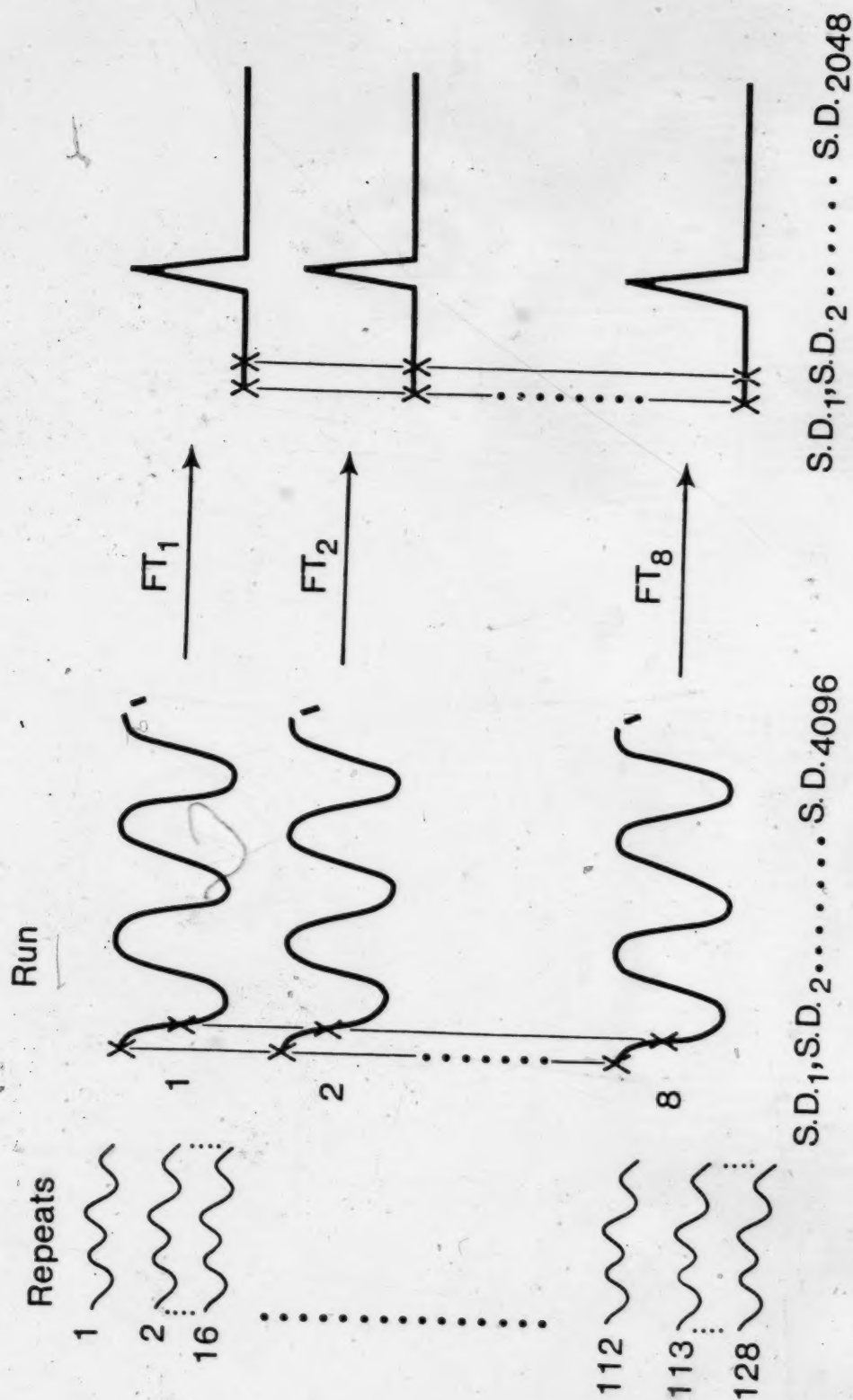


Figure 6. Schematic representation of the modality of collection of experimental data and the statistics performed on them.

D. Number of Repeats for Each Run

1. What is a measurement in FTS?

In general a measurement is defined as an independent piece of information. In analytical chemistry practice a measurement could be defined as the piece of information that produces a certain standard of analytical performance. An example could be the arbitrarily chosen time duration (often called integration time) over which we observe the analyte intensity in a DC mode in a polychromator. On the other hand this basic arbitrariness does not exist in Fourier spectroscopy. The time of one scan or mirror travel is the minimum observation unit. For instance at our experimental conditions the scan time is about 0.8 sec. This value is derived by considering an average sampling rate of 5 kHz and the fact that a scan is 4096 points long.

2. Cadmium hollow cathode lamp statistical study

The source used for this study was a cadmium hollow cathode lamp (Cathodeon Ltd. Part #30NY/Cd). The detector used was a solar blind (Hamamatsu R166) sensitive in the region between 200 to 300 nm. With this study we tried to give an answer to the following questions: What is a measurement in an interferometer system? What is the number of repeats to use in carrying out statistical studies?

A comparison was made between 7 different files obtained observing the cadmium hollow cathode lamp at the same experimental conditions. In each file the eight stored interferograms were obtained by averaging 1, 2, 4, 8, 16, 32, and 64 single scan interferograms (repeats). The emission, standard deviation and signal-to-noise ratio spectra, obtained from the files where each record is the average value of 1, 16, and 32 repeats, are shown in Figures 7, 8, and 9. The three types of spectra obtained from a file containing in each record the average value of 32 repeats with optical misalignment are shown at the bottom left of Figures 7, 8, and 9. The corresponding interferogram and interferogram standard deviation of the files described above are shown in Figures 10 and 11. The data for 32 repeats with optical misalignment is repeated to show how the perfect optical alignment is crucial to the success of the study.

Since the amount of information that these graphical-statistical data convey is enormous and therefore difficult to easily assess, it is necessary to stop a moment and think in terms of ideal spectra.

The main features of the three types of spectra should be: spectral cleanliness with no spurious spectral features at both sides of major peaks for the ideal emission spectrum, even noise distribution reflected in a

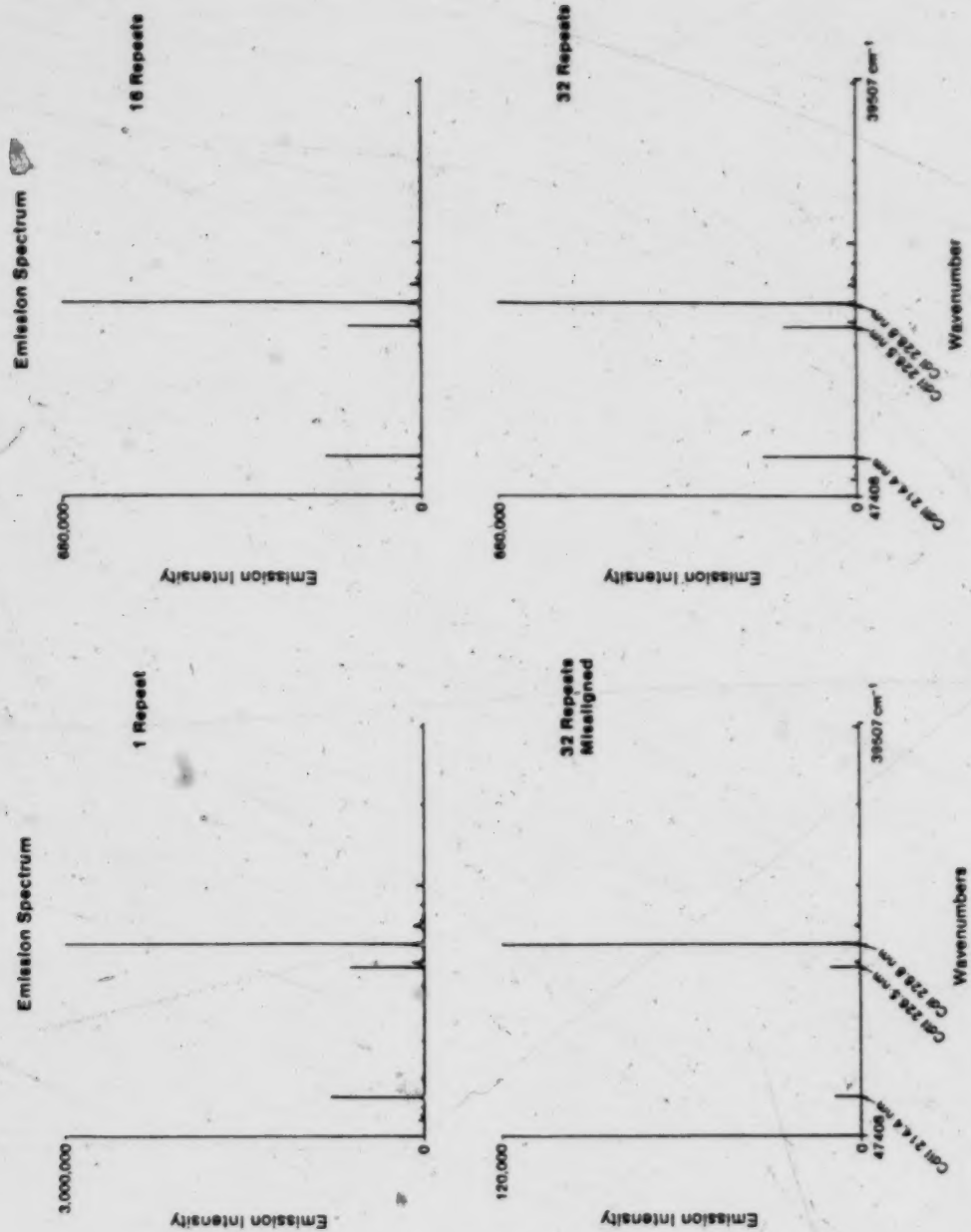


Figure 7. Emission spectra of cadmium hollow cathode lamp.



Figure 8. Standard deviation spectra of cadmium hollow cathode lamp.

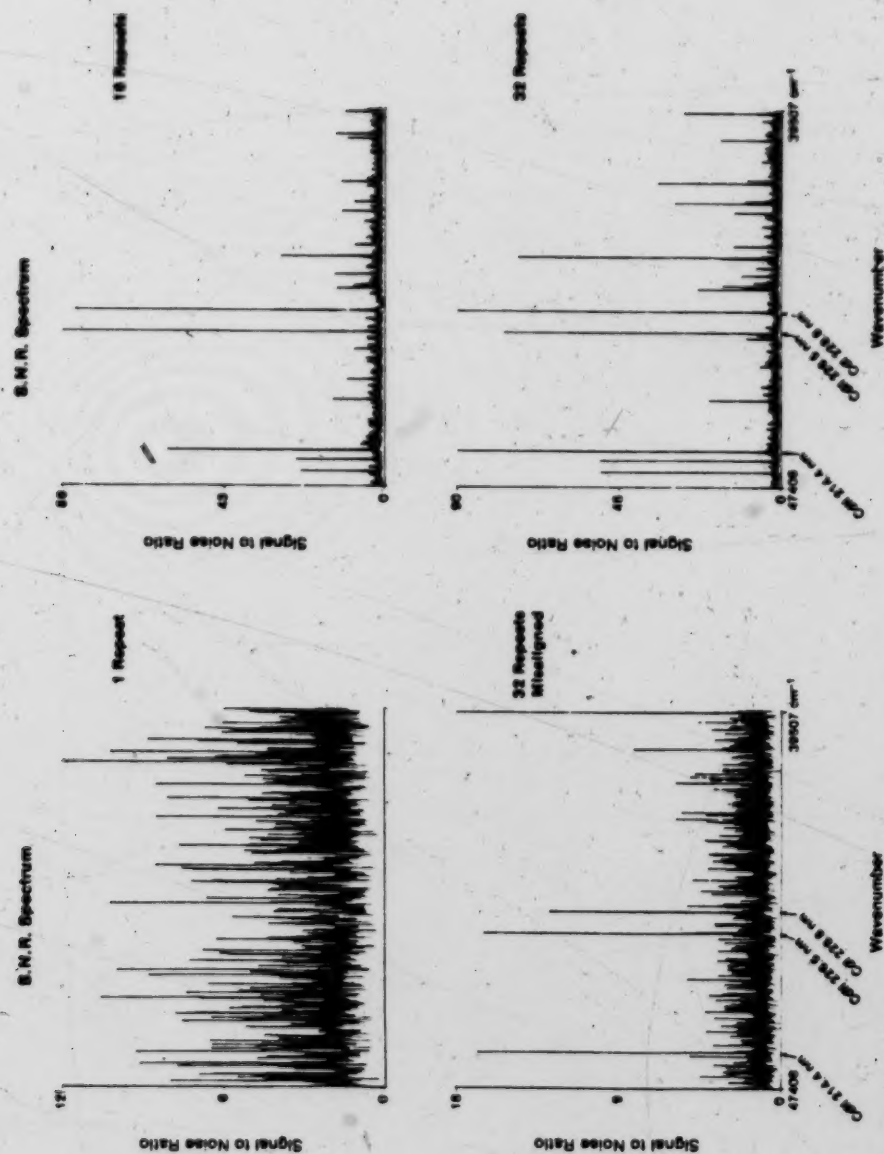


Figure 9. Signal-to-noise ratio spectra of cadmium hollow cathode lamp.

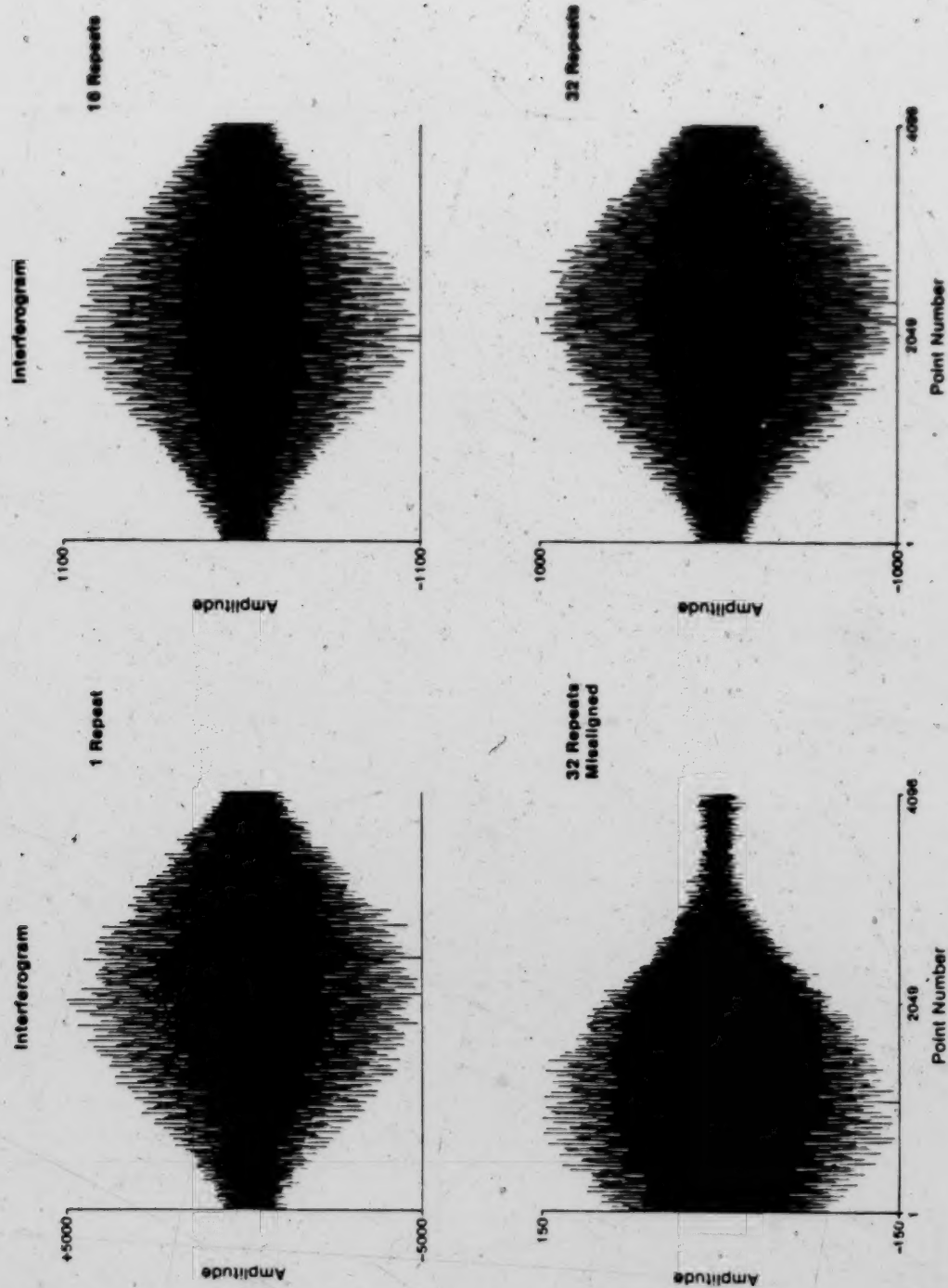


Figure 10. Amplitude interferograms of cadmium hollow cathode lamp.

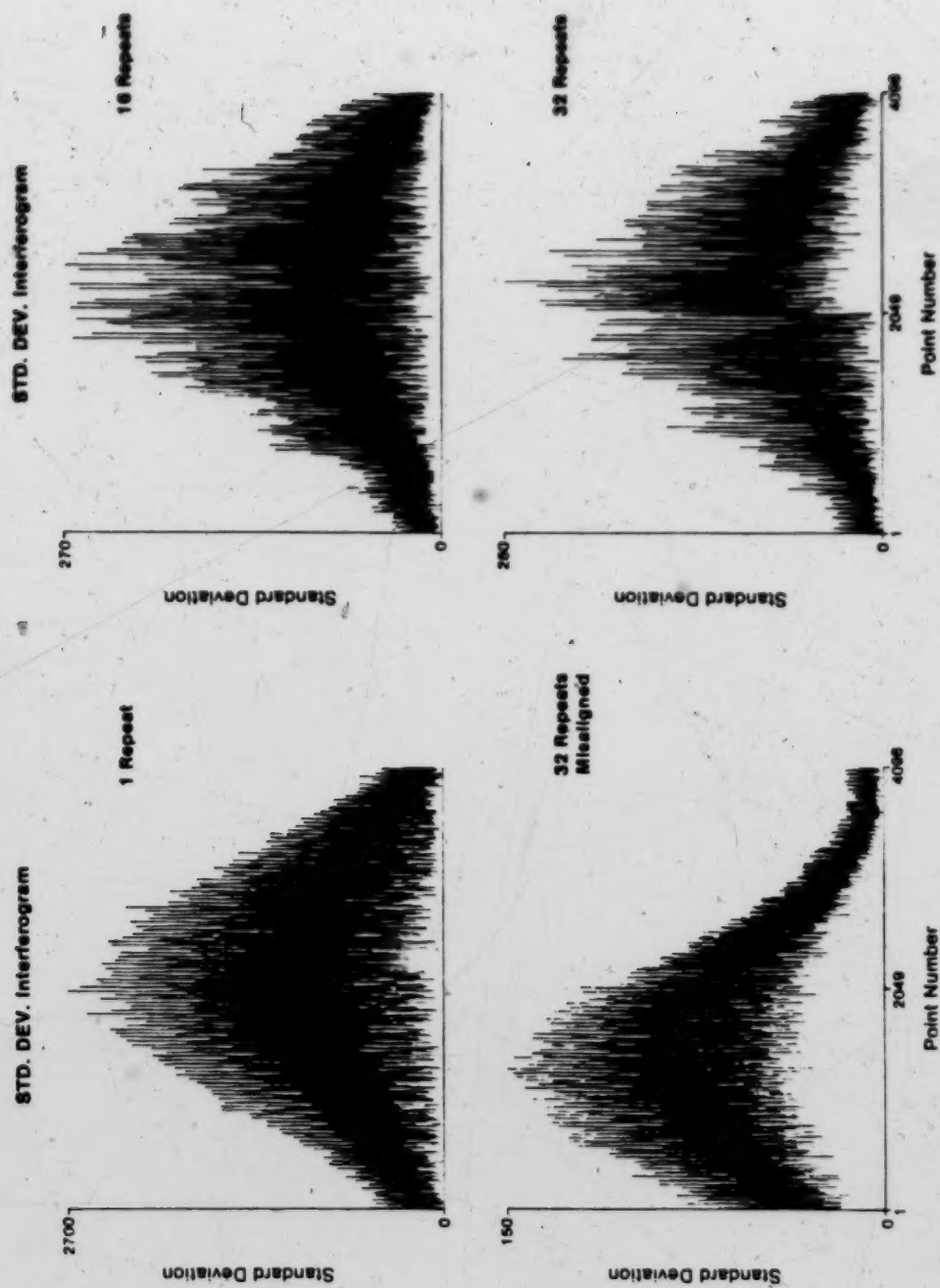


Figure 11. Standard deviation interferograms of cadmium hollow cathode lamp.

constant standard deviation value over the frequency axis for an ideal standard deviation spectrum, and coincidence in shape of ideal emission and ideal signal-to-noise ratio spectrum.

From a visual examination of the three types of spectra for the four cases shown, it is evident that the only spectra obtained from files which contain in each record the average of 16 and 32 repeats are close to the ideal case.

The emission spectra for all four cases appear closely equivalent and therefore no classification in terms of relative quality can be done. The two worst cases at the left of Figure 8 indicate a highly peak localized noise behavior. The S.N.R. spectra for the two worst cases at the left of Figure 9 have very low signal-to-noise ratio values.

In carrying out statistical studies only files containing in each record the average of 16 repeats have been used. The reasons for this choice are various:

1. The file containing in each record the average of 32 repeats (corresponding to double observation time of the case of choice) shows nearly the same signal-to-noise ratio value. Effectively in the case of each record containing the average of 32 repeats we reach a flicker noise limited situation.
- 5

2. The interferogram and the interferogram standard deviation of the file containing in each record the average of 32 repeats shows a noticeable asymmetry (Figure 10, bottom right side). It is particularly visible in the interferogram standard deviation (Figure 11, bottom right side) where a break in shape around the 2049 point is noticed.
3. On the other hand at cases in which each record contains the average of a number of repeats lower than 16 the signal-to-noise ratio at the major peak has a lower value than the case of choice.

From the standpoint of the unit of measurement these results indicate that at the experimental conditions an observation time longer than 128 repeats (8×16) has the effect of not improving the precision of measurement. To stay on the very safe side it may be prudent to stop at 64 repeats. The total observation time in this case is $64 \times 0.8 = 51$ sec. By including the time between repeats due to extra mirror movement the time for a measurement is 255 sec (~4 minutes).

CHAPTER 3

NOISE BEHAVIOR OF A FOURIER SPECTROMETER WITH A HOLLOW CATHODE LAMP AS A SOURCE

I. Introduction

Noise behavior and, in particular, its distribution along the spectral frequency axis in Fourier spectrometry is presented in this chapter using hollow cathode lamp sources. The hollow cathode lamp is a very stable source with an RSD of 0.1% [98]. Any observed fluctuation exceeding this value is due to signal destabilizing effects occurring downstream from the source in the Fourier spectrometer. These measurements constitute a baseline study to which the study of a source such as the inductively coupled plasma can be compared.

II. Experimental Conditions and Data Presentation

The following hollow cathode lamps were used as sources: magnesium (Corning, Mg 26971), multielement Cu, Pb, Sn, Zn (Westinghouse, Type WL 23109), and iron (Corning, Fe 24041). With all three lamps, a solar blind photomultiplier tube (R166, Hamamatsu T.V. Co., Ltd.) operated at a potential of 660 V was used as the

detector. This detector has its highest spectral response at 220 nm, and is down to 10% of its maximum value at 160 nm and at 300 nm.

In order to test its performance in the 200 nm to 300 nm spectral region a silicon diode detector with an active area of 2.5 mm diameter (EG&G, UV-100BQ) was also used in these measurements. This detector, which was operated with no external voltage, is sensitive from 185 to 1150 nm, with its highest spectral response at 900 nm.

The hollow cathode lamp was placed at the focus of a 15 cm focal length quartz lens and incident light was directed, through a 8 mm diameter iris aperture, to the interferometer. Experimental data were collected following the statistical procedure outlined in Chapter 2. The interferograms were apodized with a Gaussian function ($M = 2$) [99] and subsequent Fourier transformation with one level of zero filling resulted in 4096 spectral points. The spectral data are presented as emission, standard deviation and signal-to-noise ratio spectra in one single figure. For a detailed description of the actual meaning of these types of spectra refer to Chapter 2. The emission spectra are also shown separately for the purpose of representing the spectral features more clearly. Expanded versions in the emission intensity axis of the emission spectra provide a more

detailed picture of the structure of spectral peaks and background.

III. Magnesium Hollow Cathode Lamp

A. Experimental Conditions

The magnesium hollow cathode lamp was run at a current of 7 ma. The total gain resulting from the setting of the current amplifier and the low noise preamplifier was 2×10^6 . The frequency bandpass was set at 8.5 kHz on the lower frequency side (high pass filter mode) and 17.5 kHz in the high frequency side (low pass filter mode). The total information that the emission, standard deviation and signal-to-noise ratio spectra convey is accessible by their simultaneous observation. This is the reason why they are presented in a single figure.

B. Emission, Standard Deviation and Signal-to-Noise Ratio Spectra

1. Total spectrum

The emission, standard deviation and signal-to-noise ratio spectra of the magnesium hollow cathode lamp are shown in Figure 5. The main eye catching behavior noticeable from the standard deviation spectrum is the fact that the noise is not evenly distributed on the

wavenumber axis. Peak tops and pods have lower absolute precision (higher standard deviation values) than the baseline. Therefore the standard deviation spectrum has an emission spectrum-like appearance with considerable broadening at the base of peaks. Moreover small peaks, such as the ones on both sides of the largest MgI 285.2 nm peak, show a very high noise content. The same noise behavior is observed also at both sides of the low intensity MgI 202.6 nm peak (middle portion of Figure 5). In this case no peaks are visible at the corresponding locations in the emission spectrum (top portion of Figure 5).

The general aspect of the signal-to-noise ratio spectrum is that it is like the emission spectrum. All peaks appearing in the emission spectrum, with the exception of the two peaks on both sides of the MgI 285.2 nm and MgI 202.6 nm peaks are replicated in the signal-to-noise ratio spectrum. In addition to all these peaks appearing in the emission spectrum, a large number of peaks at different wavenumber values are observed in the signal-to-noise ratio spectrum (bottom portion of Figure 5). From these major observations information about the spectral components' nature and noise behavior can be deduced.

The peak localization characteristics of noise, so evident in the standard deviation spectrum, allows a clearer definition of peaks barely visible or not visible at all in the emission spectrum, such as the peaks on both sides of the MgI 202.6 nm peak. The signal-to-noise ratio spectrum permits the unequivocal differentiation between "real" peaks and spurious spectral features or incidental wiggles in the baseline to be made. In fact, if it is true that these experimental results show a larger absolute noise on spectral peak locations, it is at least logical to expect a smaller R.S.D. (relative standard deviation) in spectral locations where the signal is present. Due to the inverse reciprocity relationship, a small R.S.D. corresponds to a high signal-to-noise ratio value. This is the reason why spectral peaks of intensity so low to be only visible in expanded versions of the emission spectrum have a replicate in the signal-to-noise ratio spectrum. On the other hand, a low value in signal-to-noise ratio strongly suggests the absence of signal content. This is the case for the low intensity baseline and for the two peaks around the MgI 202.6 nm and the MgI 285.2 nm peaks. Their low signal-to-noise ratio value, practically indistinguishable from the baseline, constitutes a first indication of their spurious nature. Another very interesting feature of the signal-to-noise

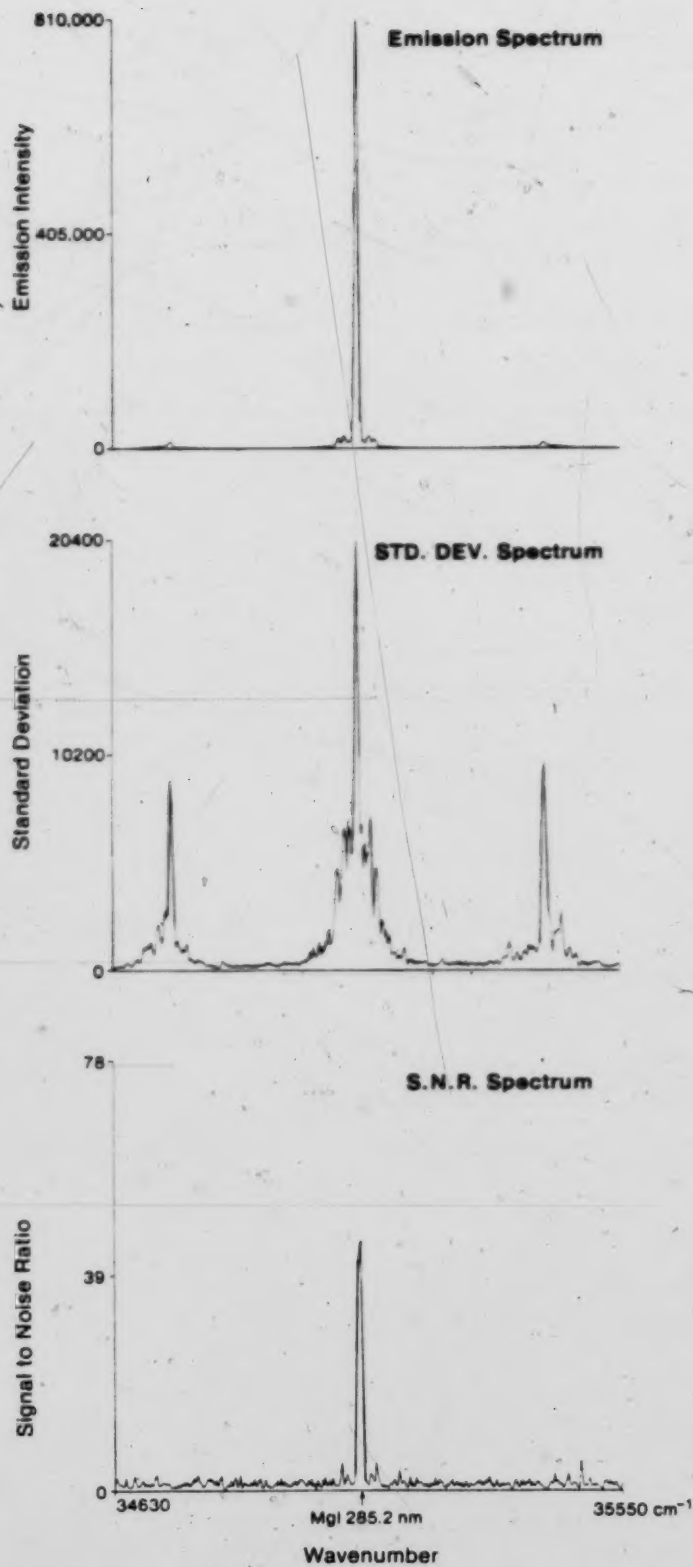
ratio spectrum is the fact that it offers a total visual "packaged" picture of the observed noise behavior. In our case almost all peaks, irrespective of their intensity, have nearly the same signal-to-noise ratio value. This is a very strong indication that the experimental noise situation under investigation is a flicker noise limited one. In the next three sections the three types of spectra for three different spectral regions will be discussed in detail.

2. Spectral region around the MgI 285.2 nm peak

The emission, standard deviation and signal-to-noise ratio spectra of the spectral region around the MgI 285.2 nm peak are shown in Figure 12.

This expanded version of the spectral region considered in the three types of spectra allows more detailed observations to be made. The shape of the MgI 285.2 nm peak resolution function is clearly visible in the emission spectrum. The presence of the two peaks on each side of the MgI 285.2 nm peak is also shown. They are at the same distance from the central peak ($\sim 360 \text{ cm}^{-1}$) and their shape is not peak-like. They do not have peak pods and are broad in shape. An extremely high standard deviation value characterizes these features and the noise content is somewhat spread on the adjacent baseline. In particular, in the case of the MgI 285.2 nm peak, the high

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noise present at the peak spreads to cover the peak pods and further. The final result is the broad noise shape at the base of the peaks. Again the extremely high noise content of the two peaks on both sides of the MgI 285.2 nm peak is reflected in its baseline-like signal-to-noise ratio value (bottom portion of Figure 12).

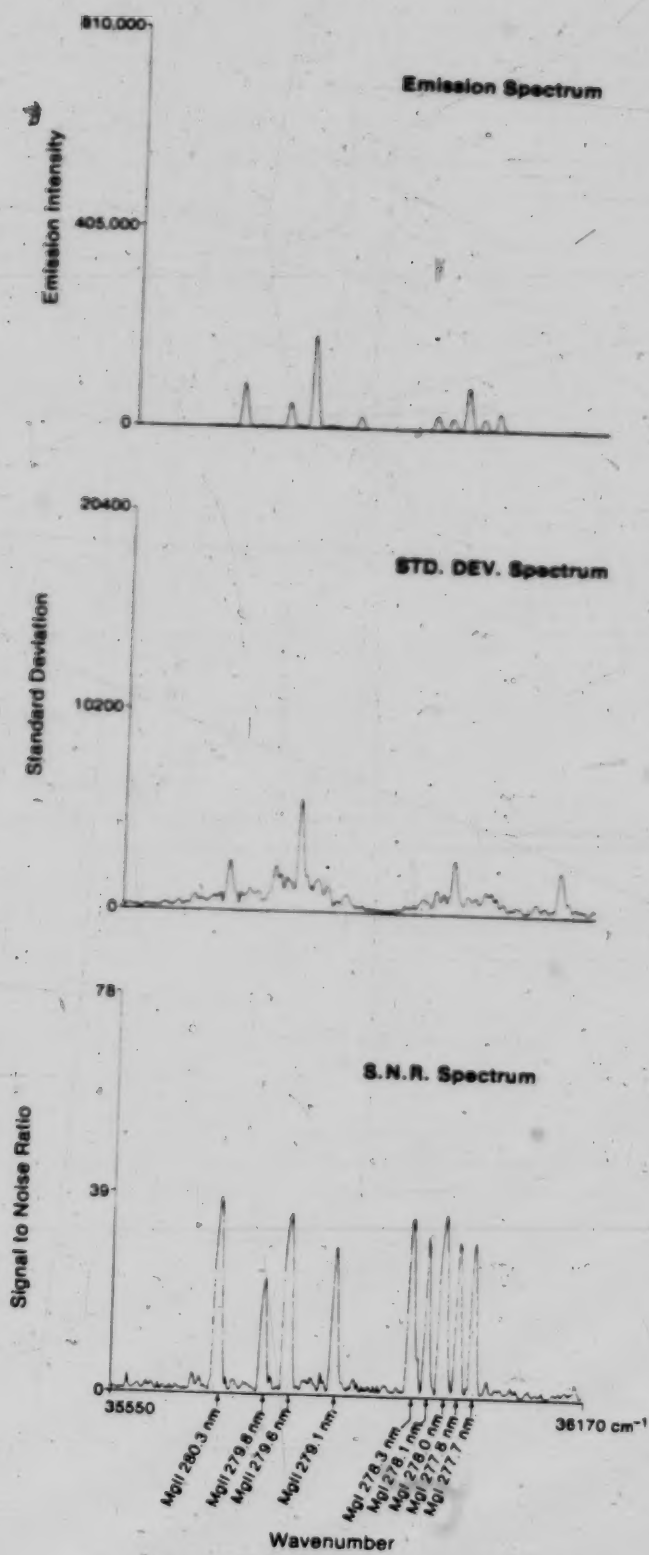
3. Spectral region from 277 to 280 nm

The emission, standard deviation and signal-to-noise ratio spectra of the spectral region from 277 to 280 nm are shown in Figure 13. In the emission spectrum shown, at the top of Figure 13, all peaks are completely resolved. This is in agreement with the fact that the theoretical resolution achievable at 280 nm is about 0.05 nm and the peaks forming the quintuplet are separated from each other by about 0.15 to 0.16 nm.

Again the characteristic peak localization of the noise is clearly visible in the standard deviation spectrum. The signal-to-noise ratio spectrum shows a levelling of all peaks at the value of about 40. This behavior indicates that for all peaks the noise increases linearly with the peak intensity therefore keeping the signal-to-noise ratio value constant, i.e. flicker noise limited situation.

A further example of how the standard deviation and the signal-to-noise ratio spectra can be used as

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diagnostic tools is illustrated by these spectra. At the top of Figure 13, at the right hand side of the quintuplet, a barely visible glitch on the baseline is present. The glitch assumes the form of a more visible peak in the expanded scale ($\times 32$) emission spectrum of the same spectral region shown in Figure 14.

Suppose we would like to find out whether this is a real peak or an error. By examining the emission spectrum we would not be able to satisfy our curiosity. On the other hand a glance at the standard deviation spectrum at our experimental conditions would confirm the presence of a spectral feature at the wavenumber value. The verification of the nature of the spectral feature is obtained through observation of the signal-to-noise ratio spectrum. In the example considered, its extremely low signal-to-noise ratio value, of the same magnitude of the background, constitutes strong indication of its spurious nature.

4. Spectral region around the MgI 202.6 nm peak

The emission, standard deviation and signal-to-noise ratio spectra of the spectral region around the MgI 202.6 nm peak are shown in Figure 15. In order to better illustrate the peak structure, the spectra cover a very narrow spectral region around the peak. The standard deviation and signal-to-noise ratio spectra are expanded

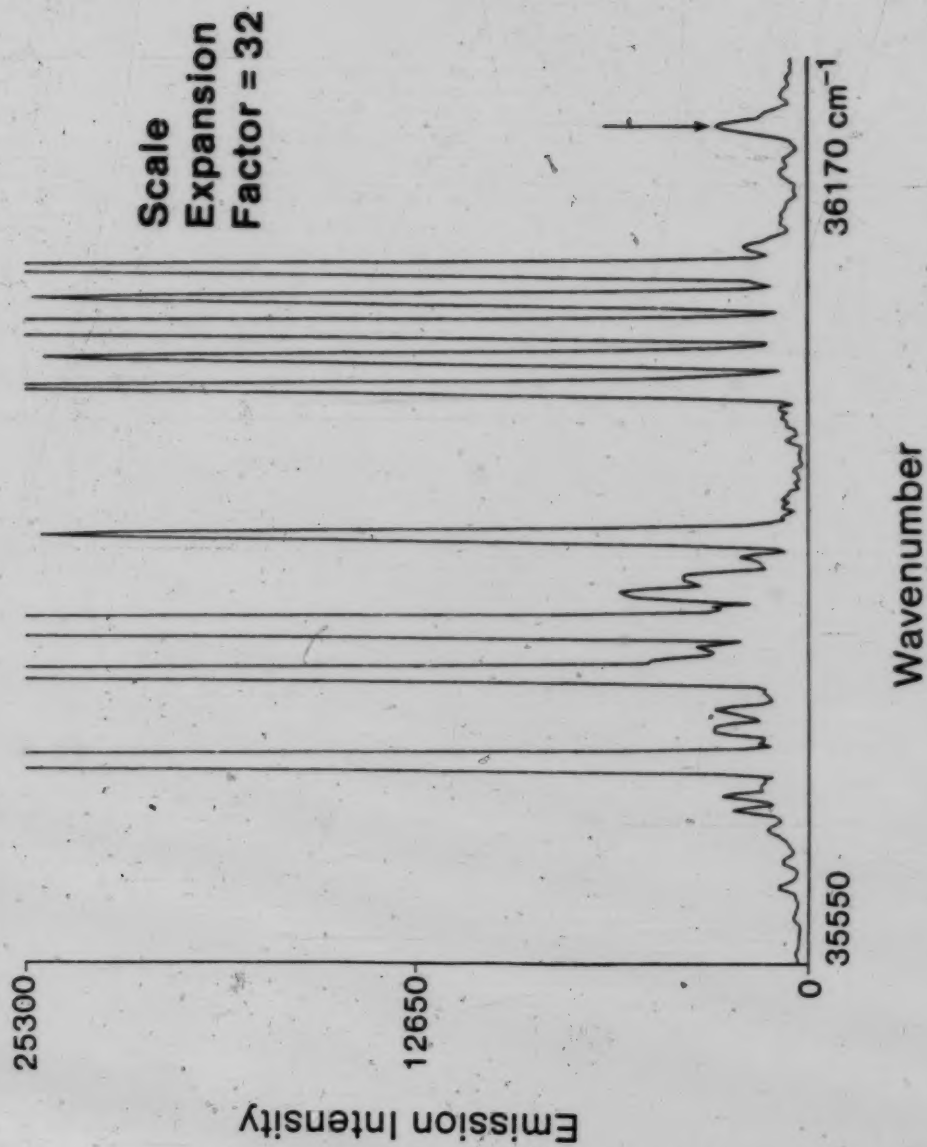
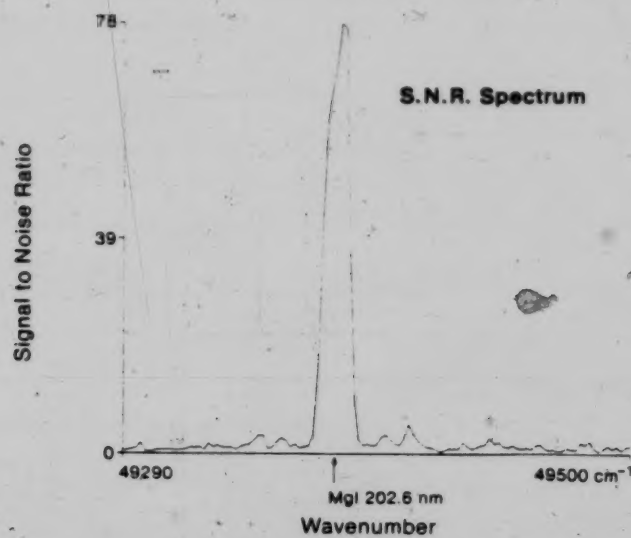
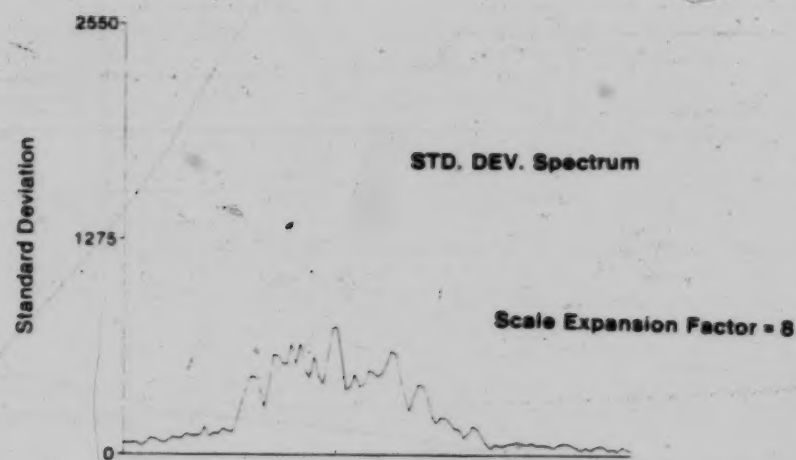
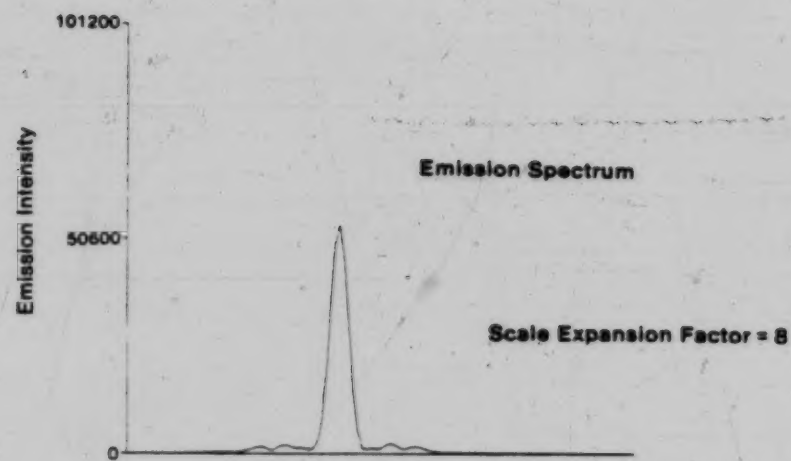


Figure 14. Magnesium hollow cathode lamp: scale expanded emission spectrum in the 277 to 280 nm spectral region.

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eight times in the intensity axis to allow a better definition of the peak features.

The first pods on each side of the central peak have a relative intensity with respect to the peak height intensity of about 4%. This value is in satisfactory agreement with the theoretical value for the Gaussian apodization (3%) with $n = 2$ [99]. In our case, in fact, the spectrum can be considered as superimposed on a spectral background of average value higher than zero. The same correspondence between theoretical value and actual experimental one is found for the peak width at half height. The observed experimental value for the MgI 202.6 nm peak is about 7 cm^{-1} and the theoretical on the basis of the resolution obtainable at the experimental conditions (8 cm^{-1}) is 6.8. In this case the noise is not chiefly localized on the peak top, like in the previous cases. It is found mainly at the peak pods, and it seems to spread more on the adjacent baseline. This translates to a higher peak signal-to-noise ratio value. No exact causes for this behavior can be found. Even if the peak noise localization is, generally speaking, a constant observed behavior, it must originate from experimental error and not be the result of factors of fundamental nature. This point will be discussed further in section D.3 of this chapter.

In the next section the spectral features appearing in the emission spectrum will be discussed in more detail.

C. Emission Spectrum

The emission spectrum of the magnesium hollow cathode lamp with the solar blind photomultiplier tube as a detector is shown in Figure 16. At the operating conditions three aliasing regions are covered. In order to distinguish the three spectral regions, a 3-character set labelling for the horizontal axis is used; the atomic lines are labelled under the same character set of the alias region to which they belong.

The "folding-over" effect of the different alias regions is reflected in the unorderly sequence by which the lines appear in the spectrum. Conspicuous is also the presence of the two spectral features at both sides of the largest intensity peak at 285.2 nm. In an expanded intensity axis version ($\times 16$) of the spectrum, which is given at the top of Figure 17, these two spectral features are more obvious. They are indicated by two arrows. At the bottom of the same figure an expanded version ($\times 256$) of the magnesium emission spectrum is provided. In this spectrum two spectral features (indicated by two arrows) at each side of the low intensity MgI 202.6 nm peak are now revealed. They are at the same distance from the central peak as those on each side of the MgI 285.2 nm

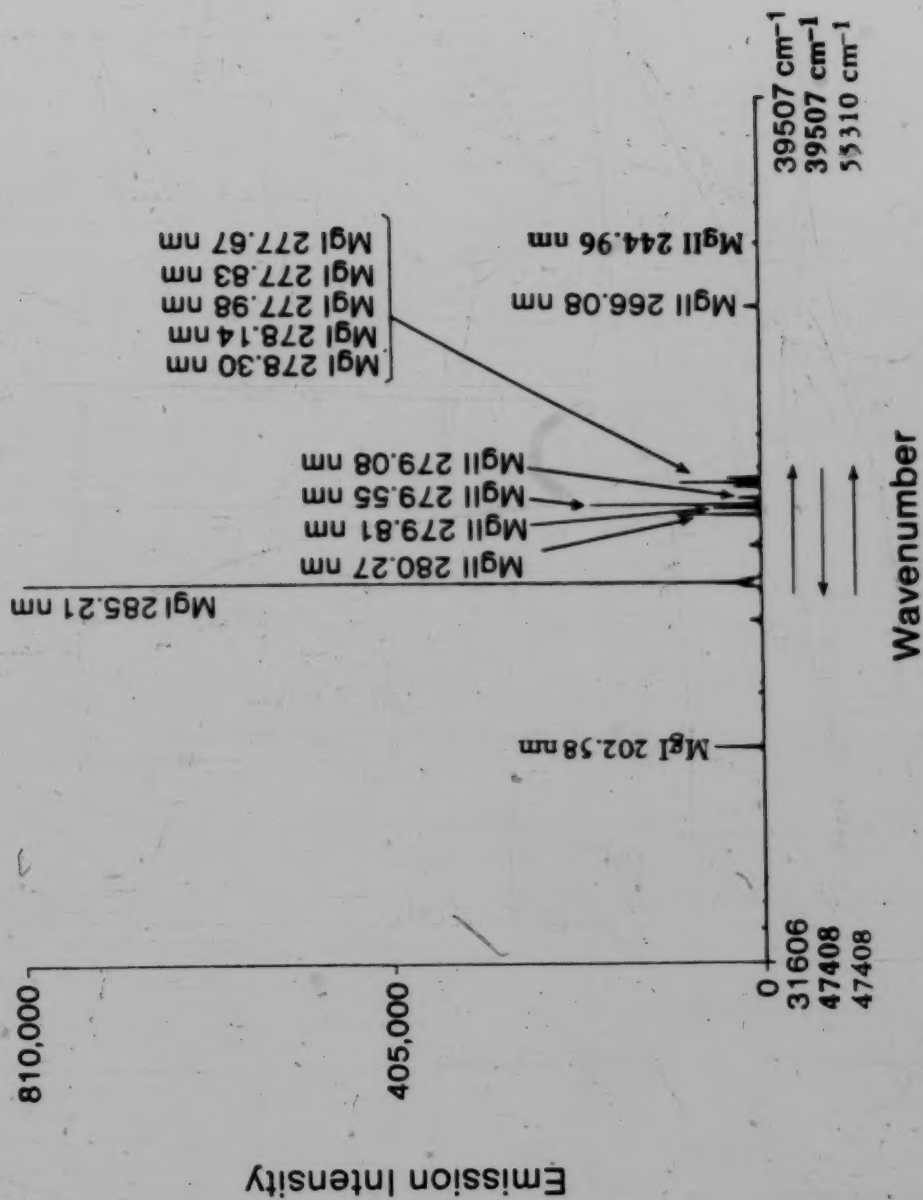


Figure 16. Magnesium hollow cathode lamp: emission spectrum in the ultraviolet spectral region.

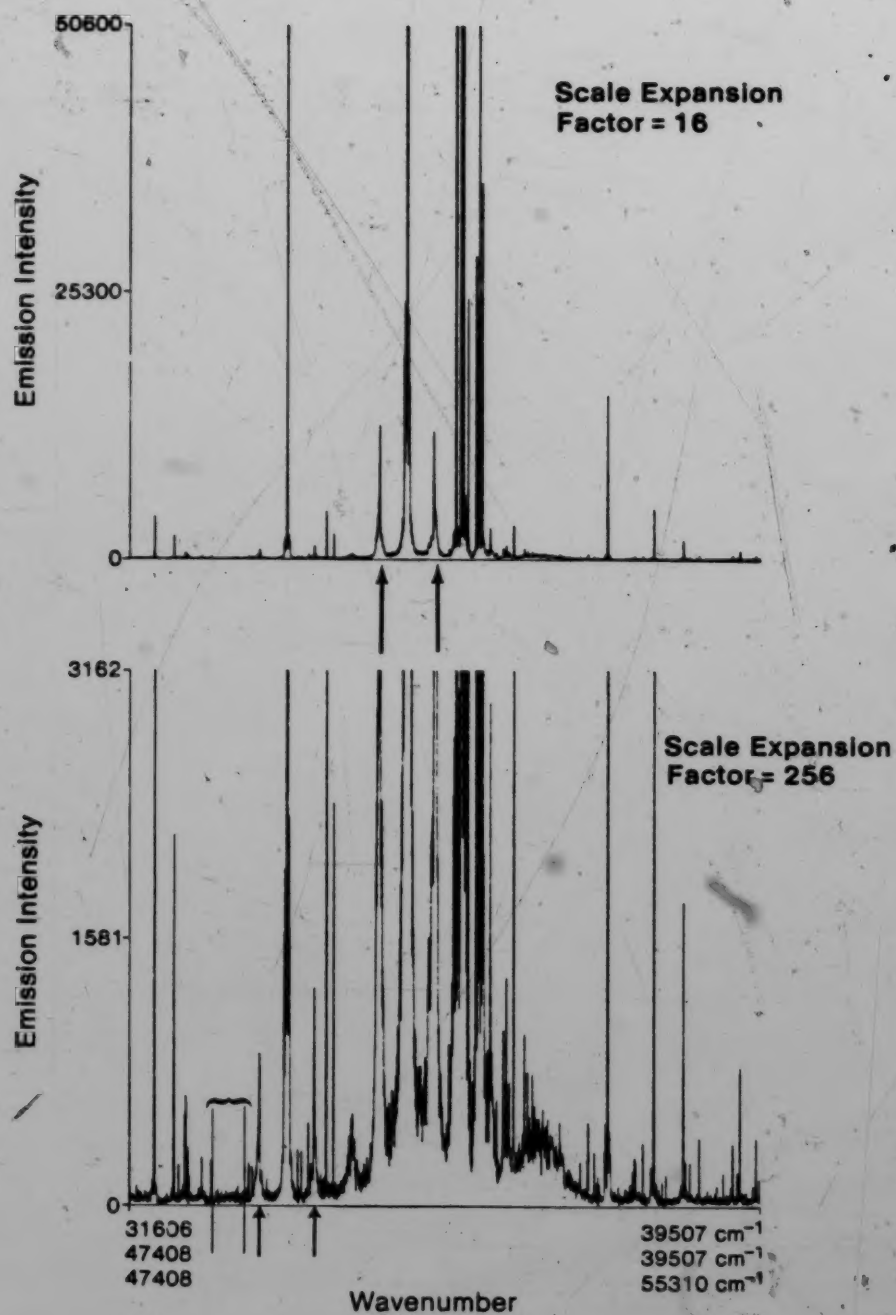


Figure 17. Magnesium hollow cathode lamp: scale expanded emission spectra in the ultraviolet spectral region.

peak (about 360 cm^{-1}); also their relative intensities with respect to the central peak are approximately the same as in the case of the MgI 285.2 nm peak. We can anticipate that these data show that these spectral features have the same origin. They are the result of an operation of multiplication-modulation of the individual spectral peaks frequencies and another frequency (or frequencies) present at the experimental conditions. This point will be discussed in detail in the next section where an attempt to find the causes of formation of the spurious spectral features will be given. Furthermore in the same spectrum the high complexity of the spectral background is also apparent. Only the spectral region enclosed by brackets appears as an absolutely spectral feature-free region.

Finally in accordance with the fact that this spectrum, like all the spectra reported in this thesis, is the result of a double sided amplitude transformation, the background shows an average value higher than zero [100].

D. Comments

1. Introduction

In this section two topics will be dealt with. An attempt to identify the probable causes of the occurrence of the spurious spectral features on each side of the MgI 285.2 nm and the MgI 202.6 nm peaks will be given. The

uneven distribution of the noise along the frequency axis, in particular its peak localized behavior which strongly contrasts with the theory [101], will be analyzed. Both discussions will provide some intuitive feel and some theoretical insight on the method of Fourier spectroscopy.

2. Spurious spectral features

At times low intensity spectral features symmetrically located with respect to the central higher intensity peak are found at practical experimental conditions. They are the result of experimental errors and are therefore spurious in nature. They have been called satellites or ghosts.

In conventional grating spectrometers they are known as Rowland ghosts and were a nuisance at the time when mechanically ruled gratings, now replaced by the holographically ruled ones, were commonly used [102].

Rowland ghosts were the result of periodic error in the lead or pitch of the high precision screw used in the ruling engine.

In an analogous way in Fourier spectroscopy a periodic error in the sampling interval produces the same effect [103]. These types of errors are the result of an operation of modulation of the spectral line frequency with the frequency determined by the periodicity of the sampling error. Therefore they manifest themselves as

very faithful miniature repetitions in shape and width of the parent line. They appear at the same distance from the parent line on both sides equal to the frequency of the sampling error and their intensity is given analytically by the product of the two frequency amplitudes divided by two [63]. Moreover, a periodic sampling error would manifest itself as a very reproducible and constant error which would have the tendency to reinforce the intensity of the satellites. The experimentally observed spectral features are at the same distance from the parent lines, and have roughly the same width of the parent lines, suggesting that they may well be satellites due to periodic sampling error. A careful observation of the experimental spectrum reveals that the distance between parent line and satellite is reproducibly about 120 Hz. This value is the result of considering that an approximate sampling rate of 5 kHz would cover a total bandwidth of 2500 Hz (Nyquist frequency) and the horizontal spectral axis is linear in units of Hertz. The value of 120 Hz ($60 \text{ Hz} \times 2$) strongly suggests that electrical noise pick up could be responsible for the spurious satellites observed in the magnesium spectrum emission.

If we accept this hypothesis another question arises. Where is the interfering noise picked up from?

It cannot originate after the detector stage because it would appear as an additive 120 Hz noise, which would, in any case, be filtered off under the experimental conditions used. The observed error is multiplicative in nature or as we previously mentioned is the result of a modulation effect. If the interfering noise originates before the detector stage, the only possible places are at the source or in the spectrometer itself.

For sake of argument let's consider that this interfering frequency is picked up at the level of the hollow cathode lamp. The 120 Hz frequency would make the lamp intensity vary with a period of 120 Hz. This situation, similar to the one shown by a modulated source before the interferometer, would produce two satellites equally spaced from the parent line. Similar satellites are visible with other sources (such as the inductively coupled plasma (refer to Chapters 4 and 5)). Therefore, the most plausible explanation is that this error originates in the spectrometer itself. Most likely the spurious satellites observed in the emission spectrum are the result of the 120 Hz pick up in the moving mirror drive coil. This type of error would affect in a periodic fashion the movement of the moving mirror and would cause a sampling error.

3. Spectral noise distribution

The reasons for the peak localization property of the noise can be found in a careful observation of the interferogram.

1. A typical interferogram is severely self apodized under our experimental conditions. Self apodization refers to the dying down of the interferogram amplitude the further we go from the zero path difference on both directions, even in the case of narrow line sources (refer to interferograms in Figure 10).
2. The individual interferogram repeats, which form a single run, show some degree of variability. They appear affected by a "drift" error which has the tendency to make them grow in one direction in an asymmetrical fashion with respect to the central point.

These experimental limitations that can be attributed for the most part to drive mirror error and overall instability of the system has the following major effects: (a) they have a multiplicative effect on the "ideal" interferogram. Their effect is similar to the operation of apodization. (b) They form a residual low frequency noise component in the interferogram.

Intuitively we can recognize that the combined effects of point (a) and (b) can lead to a bias in the noise structure along the spectral axis. The signal frequency will modulate the residual low frequency noise resulting in an effective concentration of noise in close proximity to the signal itself.

A noise behavior such as the one described here has many analogies with the one observed when stars which are affected by atmosphere turbulence, are studied.

This type of noise, which has been called scintillation noise, has been the object of mathematical modeling. Bowers [97] introduced a time-dependent factor of the atmospheric transmission and calculated the consequent effect on a two line spectrum. Even though this is a simple model its solution is extremely complicated. The solution for more complicated sources appears out of reach.

A classical practical way of reducing scintillation noise is by the internal modulation technique. With internal modulation the first derivative of the interferogram is determined rather than the interferogram itself. To achieve this, in addition to the movement of the moving mirror needed to generate the interferogram, the fixed mirror is "jittered" rapidly back and forth. This effectively removes any constant term (or DC level

term) in the original interferogram before transformation. A very detailed theoretical and practical explanation of internal modulation can be found in the literature [104-105].

IV. Multielement Hollow Cathode Lamp

A. Experimental Conditions

The multielement Cu, Pb, Sn and Zn hollow cathode lamp was run with a current of 7 ma. The total gain was set at 5×10^8 . The experimental bandpass used was set from 12 to 18.5 kHz.

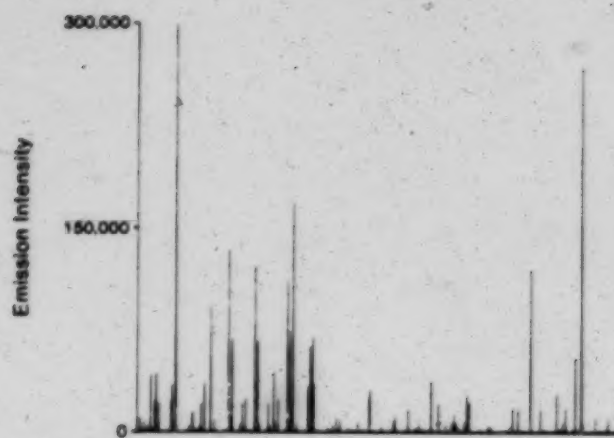
B. Spectra with the Solar Blind Photomultiplier Tube

The emission, standard deviation and signal-to-noise ratio spectra of the multielement hollow cathode with the solar blind photomultiplier tube as a detector are shown in Figure 18. Again the peak noise localization is observed in the standard deviation spectrum along with the characteristic emission spectrum-like appearance of the signal-to-noise ratio spectrum.

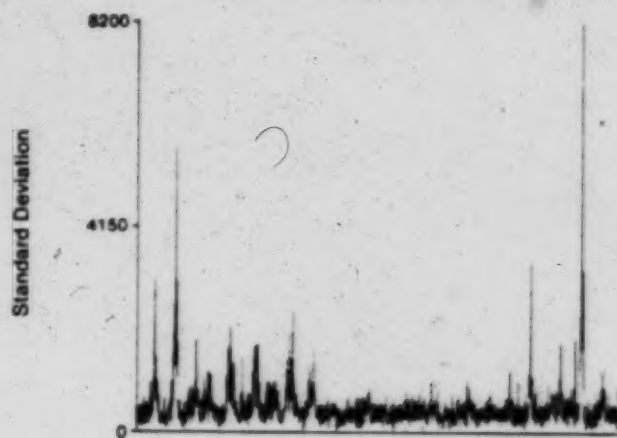
The emission spectrum at the top of Figure 18 is expanded in the horizontal axis and subdivided in 4 spectral portions (Figure 19a,b,c,d). The purpose is to illustrate one of the most interesting characteristics of laser referenced Fourier spectrometry: the wavelength

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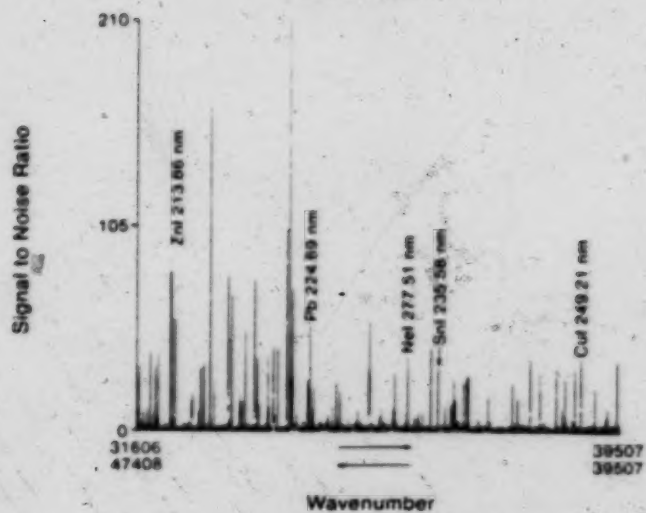
Emission Spectrum



STD. DEV. Spectrum



S.N.R. Spectrum



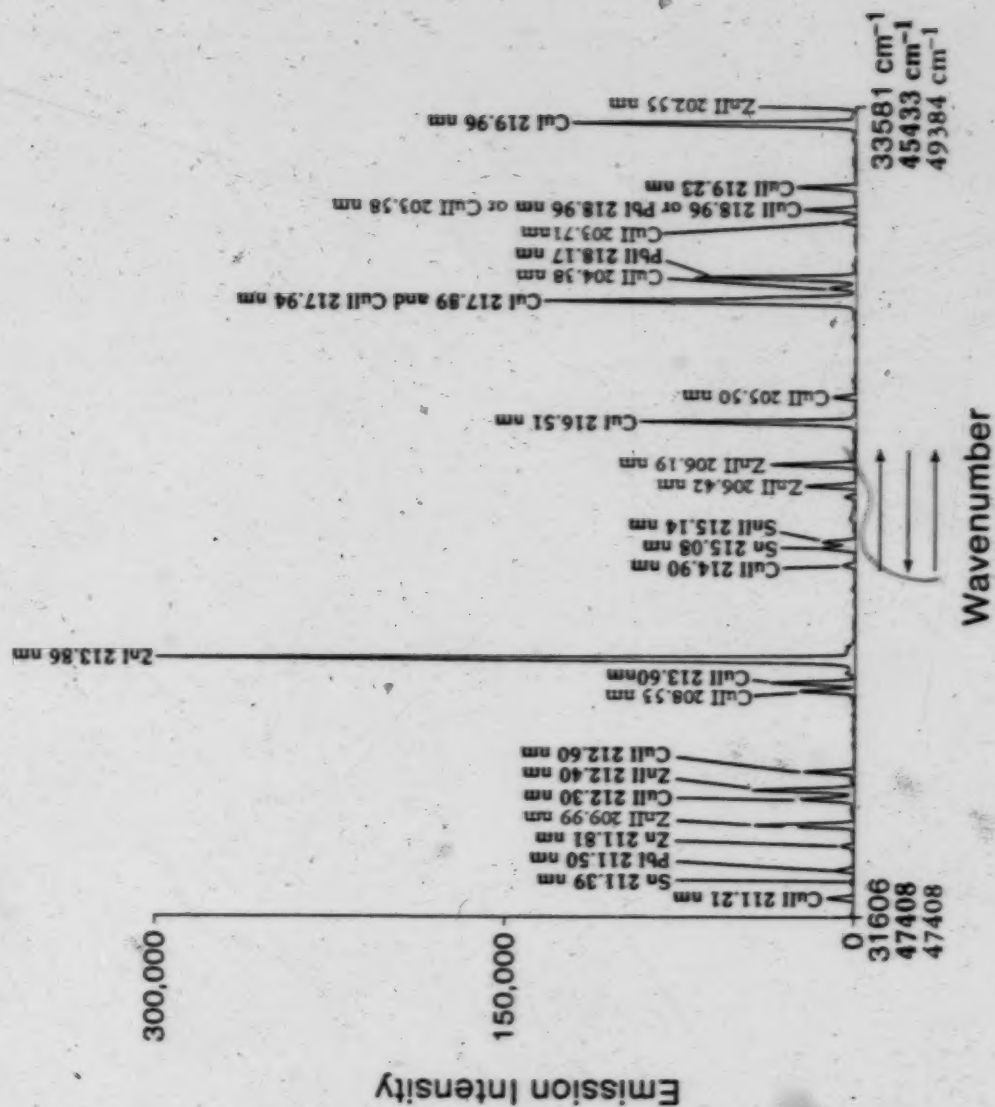


Figure 19. (a) Multielement hollow cathode lamp: emission spectrum obtained with the solar blind photomultiplier as the detector, part 1.

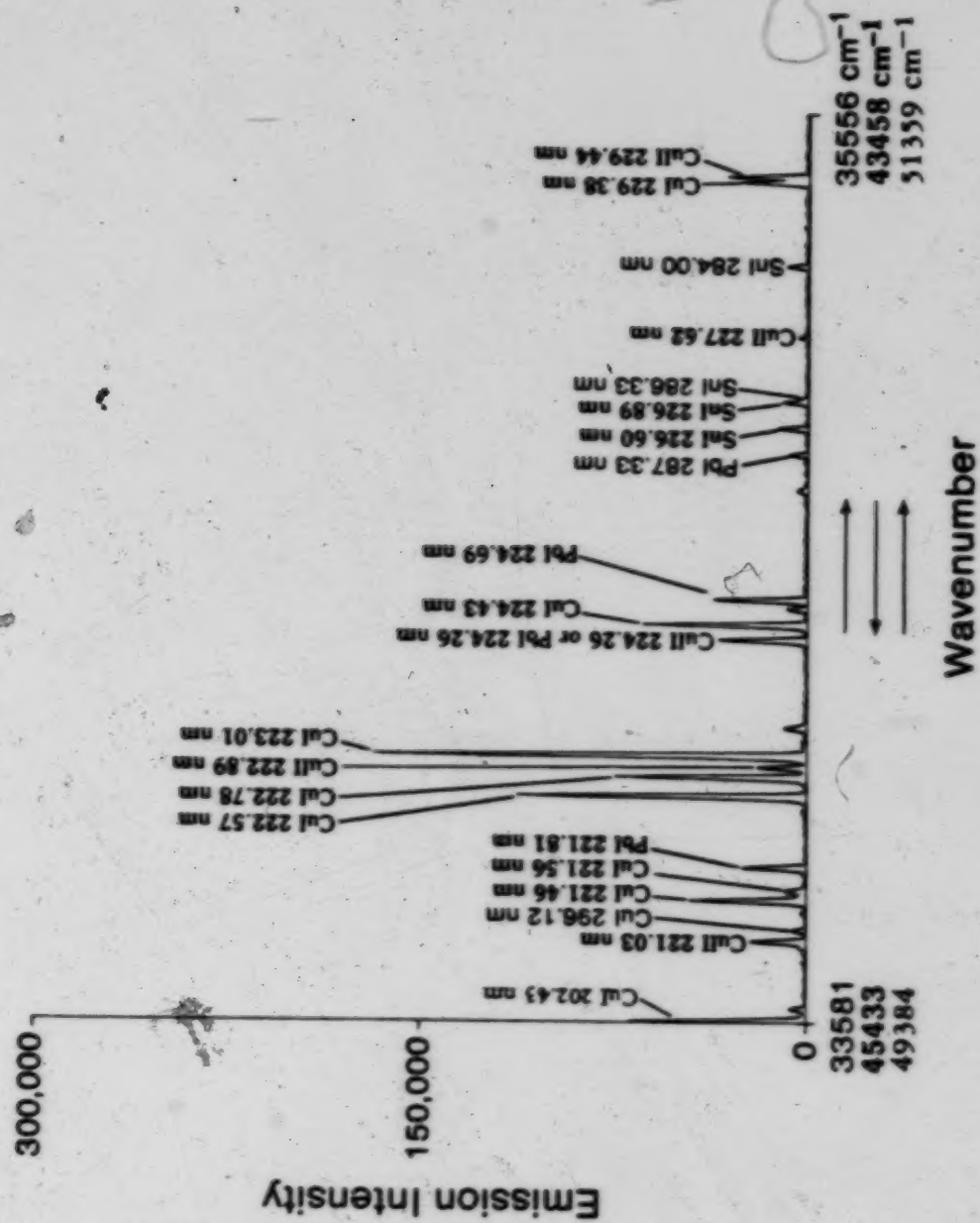


Figure 19. (b) Multielement hollow cathode lamp: emission spectrum obtained with the solar blind photomultiplier as the detector part 2.

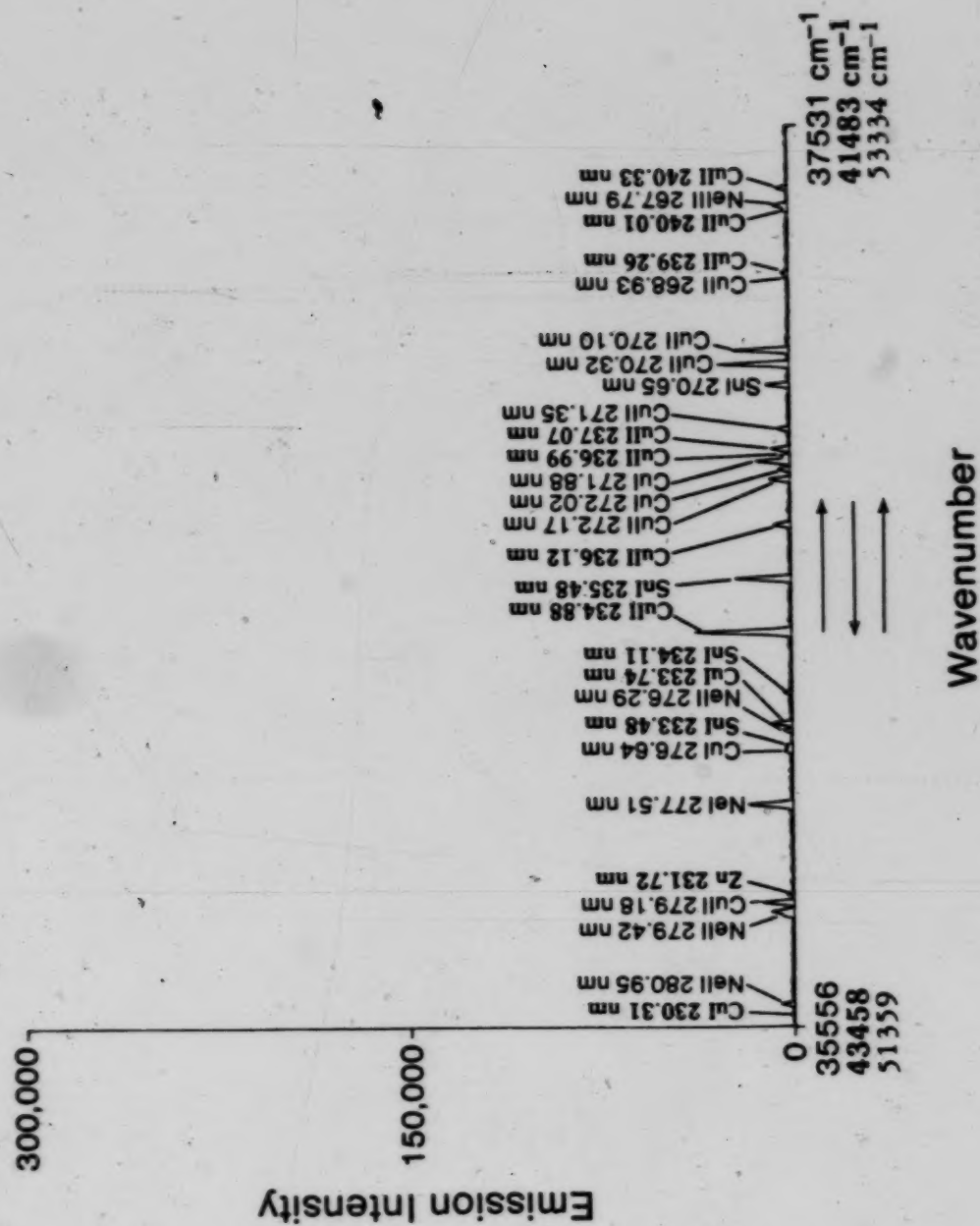


Figure 19. (c) Multielement hollow cathode lamp: emission spectrum obtained with the solar blind photomultiplier as the detector, part 3.

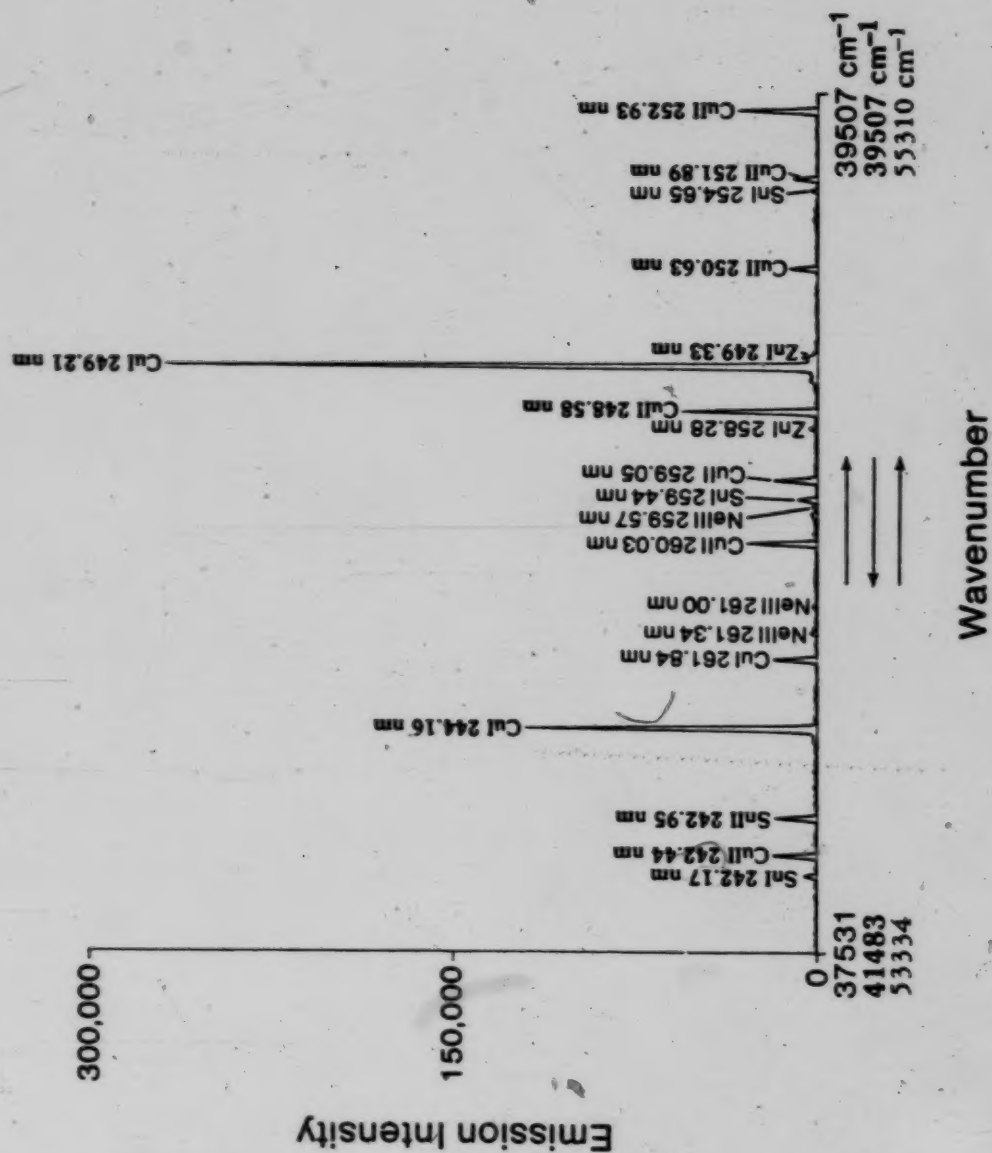


Figure 19. (d) Multielement hollow cathode lamp: emission spectrum obtained with the solar blind photomultiplier as the detector, part 4.

accuracy or what has been called Conne's advantage, which allows the identification of the spectral peaks present in the emission spectrum.

A three-character set-three aliasing region code was used and a total of 95 spectral lines of the four elements copper, lead, tin, and zinc plus neon were identified. The peaks were labelled by using the values reported in the spectral atlas Zeidel et al. "Tables of Spectral Lines" [106].

No systematic calibration, involving the matching of the optical paths of the laser and the signal, was carried out. Nevertheless the difference in wavenumber between the literature values and the experimentally observed ones were a very close ± 2 to 3 wavenumbers apart. It was impossible to distinguish the CuII and PbI peaks at 224.26 nm (Figure 19b) and the CuII and PbI at 218.96 nm (Figure 19a) because of their perfect coincidence in wavelength value. It was also impossible to tell the two peaks at 218.96 nm apart from the CuII 203.58 nm. The reason is that the two wavelength values belong to different alias regions and they incidentally fall exactly on the same horizontal axis point.

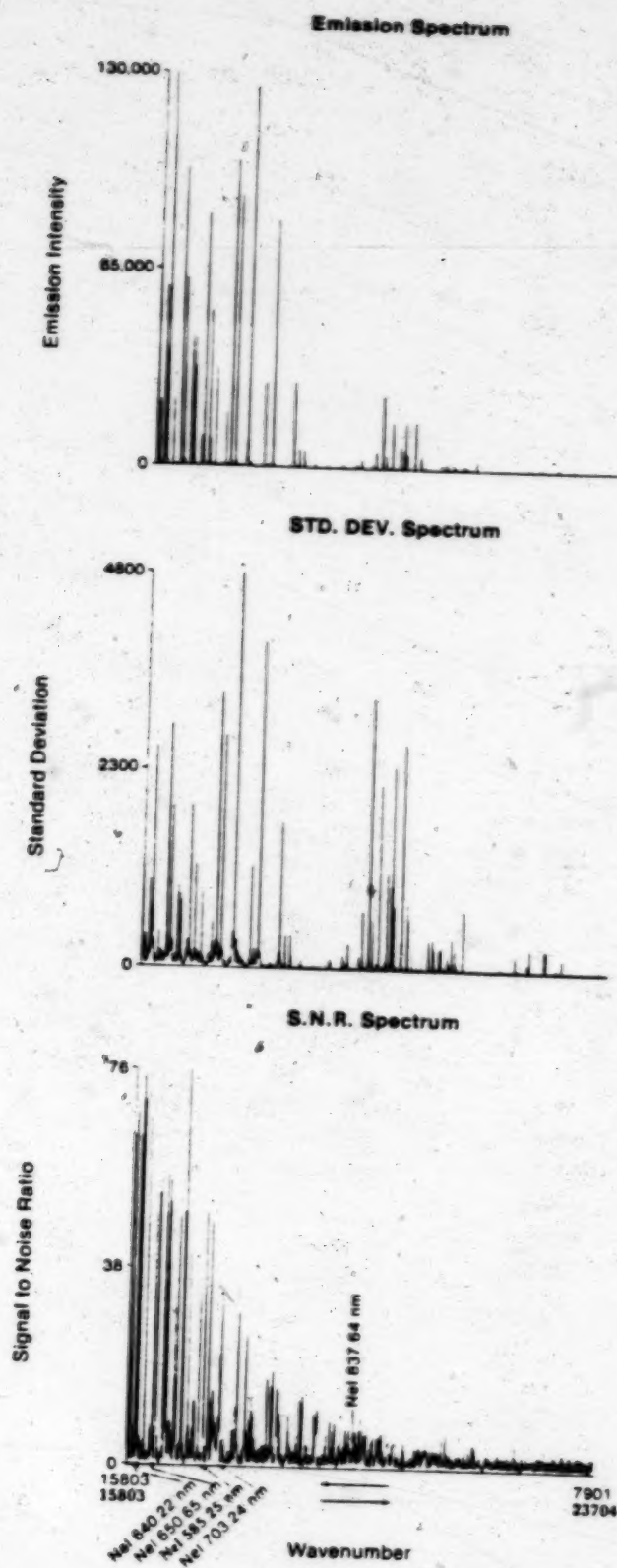
C. Spectra with the Silicon Diode Detector and Comparison
with Those Obtained with the Solar Blind
Photomultiplier Tube

The emission, standard deviation and signal-to-noise ratio spectra of the multi-element hollow cathode lamp with the silicon diode as a detector are shown in Figure 20. The emission spectra on top of Figures 18 and 20 show a totally different spectral structure.

The silicon diode detector has a much larger spectral response than the solar blind photomultiplier tube. It has also a spectral response that improves in the near infrared, therefore it is far more sensitive to a great number of neon lines than to the lines of the elements copper, lead, tin, and zinc which fall in the region between 200 and 300 nm.

Another way to look at this practical experimental problem in Fourier spectroscopy is the following. In the case of the silicon diode, the dynamic range of the analog-to-digital converter is filled with the light emitted by the more sensitive lines and the least sensitive ones fall below the resolution of the analog-to-digital converter and cannot be detected. In the situation described the silicon diode performs rather poorly.

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V. Iron Hollow Cathode Lamp

A. Experimental Conditions

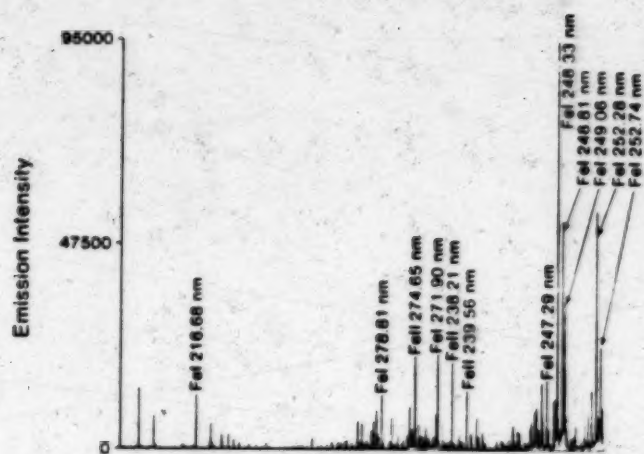
The common experimental conditions for the two emission spectra appearing at the top of Figures 21 and 22 were the following: lamp current, 10 mA; frequency bandwidth, 12-18.5 kHz. The gain was set at 1×10^7 for the spectrum at the top of Figure 21 whereas for the one at the top of Figure 22, which was the result of a partially clipped interferogram, the gain was set at 5×10^7 .

B. Comparison of Spectra

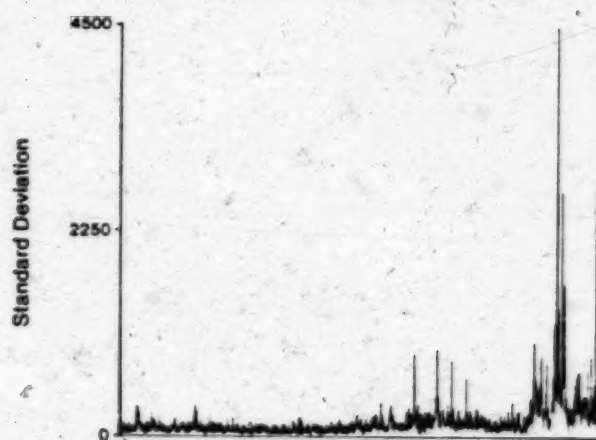
With the exception of the emission intensity values, the two emission spectra seem very similar. The two standard deviation spectra don't seem radically different either, but a great deal of dissimilarity is present in the signal-to-noise ratio spectra. The peaks on the right side of the spectrum in Figure 22 appear very noisy (low signal-to-noise ratio value) whereas the signal-to-noise ratio value for the same peaks in the spectrum in Figure 21 is rather respectable. The totally different aspect of the standard deviation and S/N spectra suggests the presence of a very different noise behavior in the two emission spectra. No unique or specific cause for the occurrence of different noise behavior in the second

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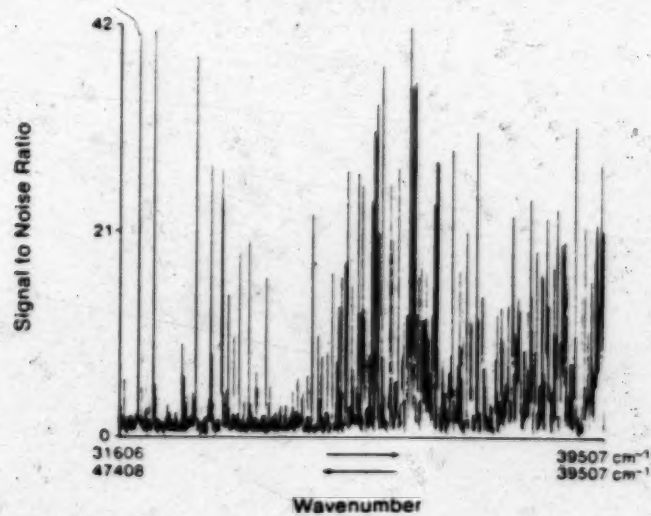
Emission Spectrum



STD. DEV. Spectrum

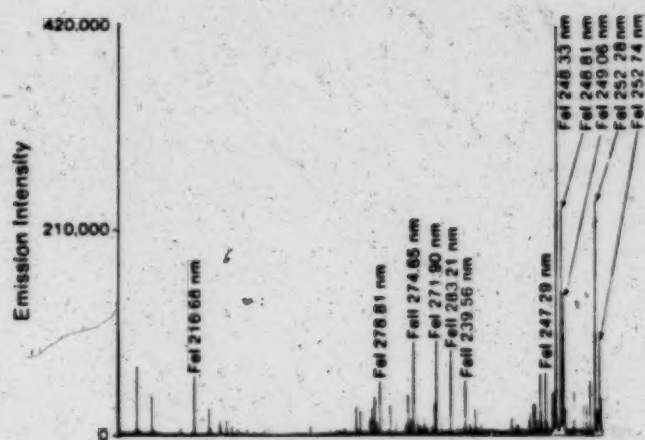


S.N.R. Spectrum

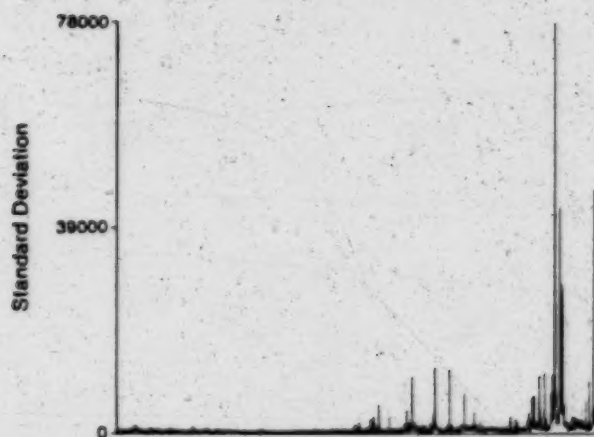


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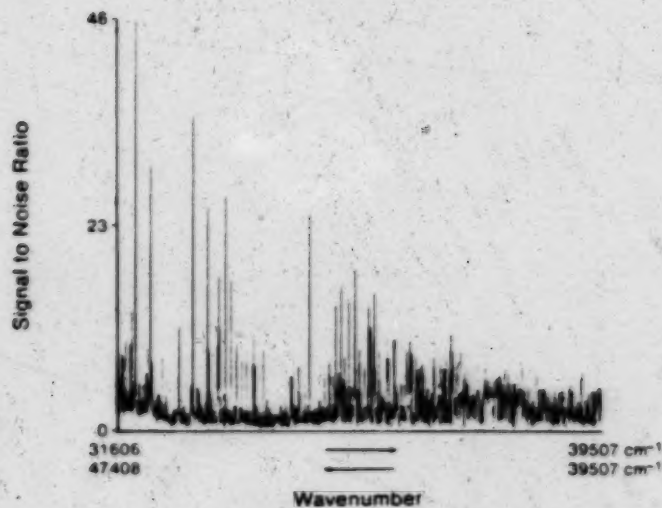
Emission Spectrum



STD. DEV. Spectrum



S.N.R. Spectrum



spectrum (Figure 22) with respect to the first one (Figure 21) can be found. The causes for this observed difference may be several: partial optical misalignment, clipping effects and noises or disturbances of electrical, mechanical or optical nature.

The simple observation of the emission spectrum does not clearly give any hint of the different qualities of the two spectra. On the other hand the standard deviation and signal-to-noise ratio spectra provide a vast amount of information and a visual representation of the quality of the emission spectrum.

VI. Conclusions

The main conclusions which can be drawn from the data presented in this chapter can be summarized in the following points:

1. Noise values consistently exceeding the intrinsic instability of the source are observed. The spectrometer itself is responsible for the degradation of the quality of the signal.
2. Strongly contrasting with the theory, a great deal of variability in the noise content is observed in spectral peaks, spurious spectral features and background.

3. At the experimental conditions spurious spectral features due to the modulation between signal frequencies and 120 Hz line pick-up in the moving mirror drive coil are observed.
4. The standard deviation and signal-to-noise ratio spectra offer detailed information about the quality of the data collected and experimental and instrumental errors which may be present.
5. Fourier transform spectroscopy is an excellent qualitative technique and allows the simultaneous observation and identification of all detectable spectral peaks.

In the next chapter a new dimension will be added to the study of the noise behavior. The noise as a function of the emission intensity along an analytical calibration curve using the inductively coupled plasma as an atomic emission source will be studied in detail.

CHAPTER 4

NOISE BEHAVIOR AND QUANTITATIVE PERFORMANCE OF A FOURIER SPECTROMETER WITH AN INDUCTIVELY COUPLED PLASMA PART I. CALIBRATION CURVE AND INTERNAL STANDARD

I. Introduction

The study of noise behavior and quantitative performance along the analytical calibration curve as measured with a Fourier spectrometer with an inductively coupled plasma as a source is the main subject discussed in this chapter. The noise behavior is described in a detailed fashion at the analyte peaks as well as along the background baseline. The classical technique of internal standardization as a means of improving the signal-to-noise characteristics of the analyte will also be reported in this chapter.

II. Experimental Conditions

The source used in this study was a 27.12 MHz radiofrequency inductively coupled plasma (Plasma Therm Inc., Kresson, N.J.). Four components made up the source: a 2.5 kW RF generator (Model HFP-25000), an automatic power control (Model ADCS-3), an automatic

matching network (Model AMN-2500E), and a plasma torch assembly (Model PT-2500). The plasma was run at the conditions reported in Table 4.

To ensure the maximum experimental reproducibility the argon plasma flow rates and nebulizer flow rate were continuously monitored. In particular the auxiliary argon and the coolant argon were connected to two flow meter control units (Matheson, #603 and #605) and throughout the whole study were constantly kept at the values indicated in Table 4).

The optical coupling between the source and the spectrometer was achieved by placing a 30 cm focal length quartz lens at its focal length from the plasma. Collimated light was directed into the interferometer through a variable aperture set at a diameter of 8 mm.

The detector used was the solar blind photomultiplier tube (R166, Hamamatsu T.V. Co. Ltd.) operated at the potential of 660 V. Unapodized interferograms were transformed without zero filling, resulting in 2048 spectral points. The reason for not using in the study described in this chapter any smoothing technique, such as apodization and zero filling, was to ensure in a given spectrum statistical independence of all spectral points [107]. For each solution a statistical set of data was collected in the manner described in Chapter 2.

Table 4
Plasma Running Conditions

		Flow meter Control setting
Power	1.5 kW	
Coolant Argon Plasma Flowrate	~15 Lpm	41
Auxiliary Argon Plasma Flowrate	~1 Lpm	20
Nebulizer Flowrate	0.8 Lpm	
Observation Height	15 mm	

III. Quantitative Study of Magnesium

A. Introduction and Experimental Conditions

Nine solutions of magnesium of concentration ranging from 0.2 to 100 ppm were aspirated into the ICP. The reasons for choosing magnesium as the analyte are several:

1. Magnesium is a well behaved element in the ICP and it shows two peaks of relatively high sensitivity in the ultraviolet region.
2. Magnesium interferograms, being formed largely by just two frequencies, are easy to monitor for shape and symmetry.
3. A solution of 10 ppm was used as a standard for this study and the one described in the next chapter.

The last point deserves a further explanation. Between sets of measurements at different concentrations of analyte a solution of 10 ppm was aspirated into the ICP to check for stability of experimental conditions. The characteristics and parameters monitored were shape and intensity of interferogram and peak emission intensity and standard deviation of the largest peaks. At any line the maximum fluctuation of peak intensity allowed for the peak MgII 279.6 nm was about 1.5% for the 10 ppm solution. This precision level has been chosen because it has been found an acceptable and reproducible value to be attained.

under normal experimental conditions. If at any time this value of fluctuation was exceeded the original precision was regained by very minor readjustments of the fixed mirror position of the spectrometer. The adoption of this tedious procedure proved to be necessary to insure reproducibility and stability of experimental conditions during the whole course of this study and the one described in the next chapter.

The concentrations of the analyte, precisely 0.2, 0.6, 1, 2, 6, 10, 20, 60, and 100 ppm were chosen to provide (a) approximately 3 orders of magnitude in concentration of analyte, (b) 3 solutions at different concentration of analyte for each order of magnitude and (c) a range of concentrations in analyte that appear equidistant in a logarithmic plot.

The experimental parameter values used in this study are reported in Table 5. The work described in the next chapter has been executed at the same experimental conditions.

B. Emission, Standard Deviation and Signal-to-Noise Ratio Spectra

The emission spectrum of a 10 ppm solution of magnesium in the ultraviolet region is shown in Figure 23. This spectrum is noticeably different from the one of the magnesium hollow cathode lamp in the same spectral

Table 5
Experimental Conditions

Voltage Solar Blind PMT	660 V
Electronic Gain	2×10^5
Filtering Conditions	10.0 - 21.5 kHz

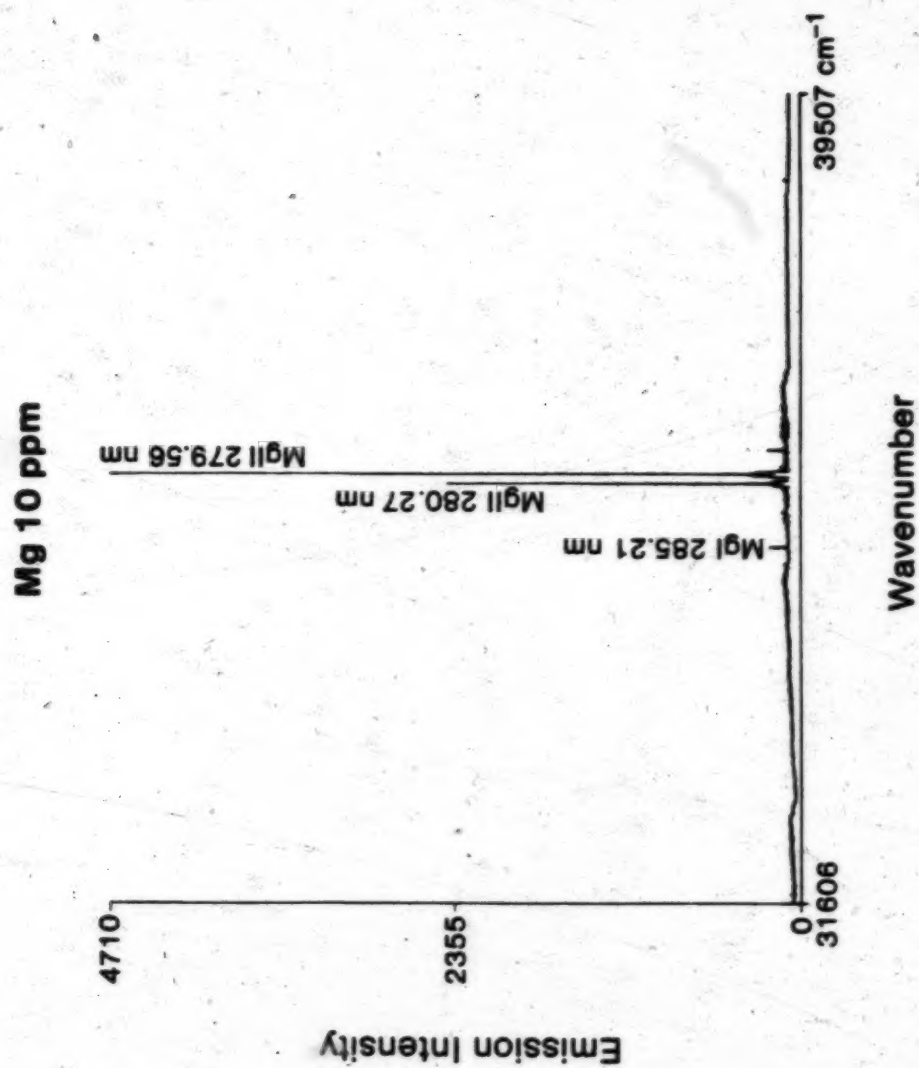


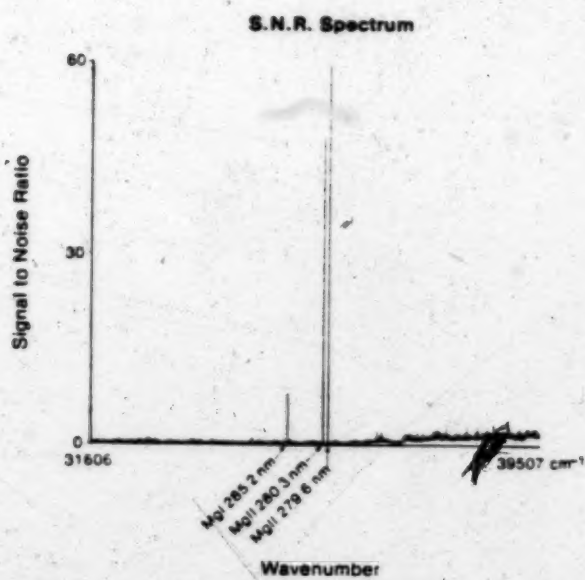
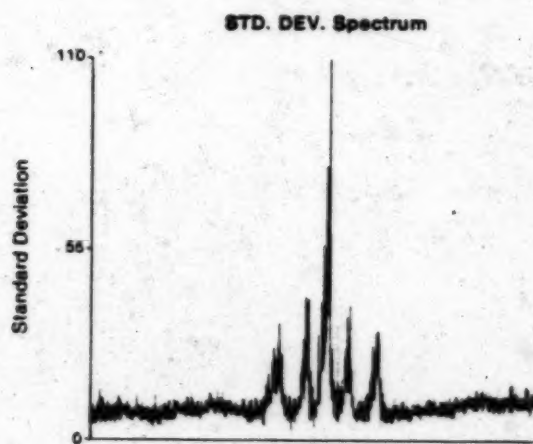
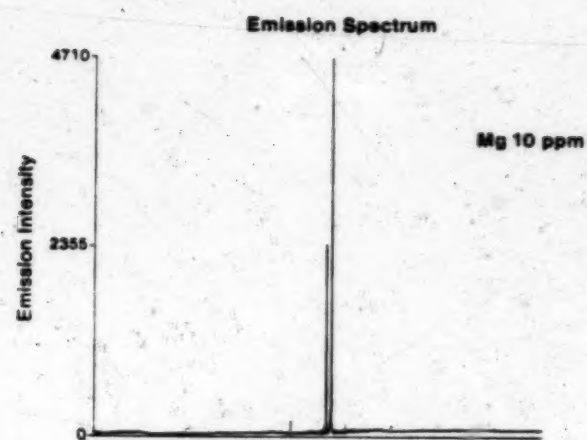
Figure 23. Emission spectrum of a solution containing 10 ppm of magnesium in the ultraviolet spectral region.

region (Figure 16). It is far less complex: it shows only two major peaks due to ionic emission, the MgII 279.6 nm and the MgII 280.3 nm. Another difference is the structure present in the background. In the standard deviation and signal-to-noise ratio spectra of the 10 ppm solution of magnesium, which are shown with the emission spectrum in Figure 24, characteristics similar to the ones observed in the magnesium hollow cathode lamp spectra are noticed.

The standard deviation values are higher at the two major peaks and around them than in the background. Since the two major peaks are very close to one another, some merging effect of the noises originated from both peaks results in a unique broad structure of noise. This broadening is more pronounced than in the case of the magnesium hollow cathode lamp (medium portion of Figure 24).

Four noisy broad spectral features (two on each side of the major peaks) are noticed in the standard deviation spectrum. They appear at wavenumber values where no spectral peaks are observed in the emission spectrum and in the signal-to-noise spectrum as well. This fact constitutes a strong indication of their spurious nature. Other indications that these spectral features are the result of modulation of the frequencies of the

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spectral peaks with other extraneous frequencies are:

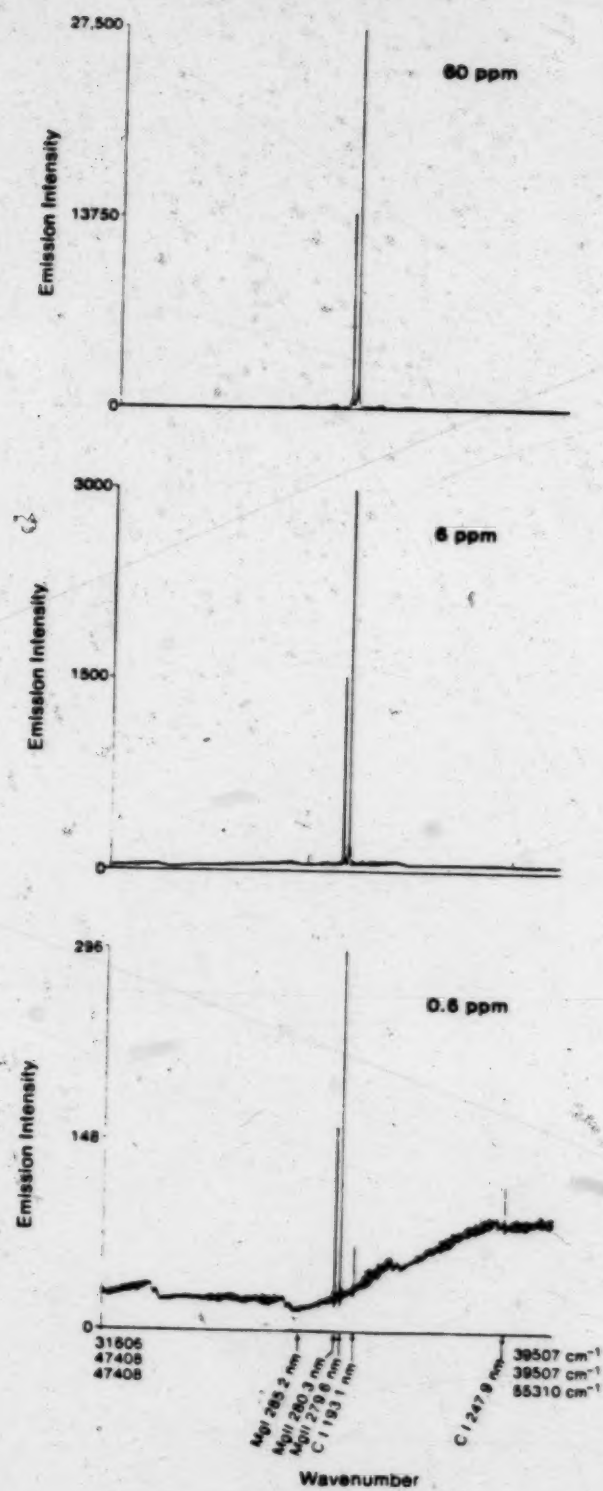
1. Their multiplicative nature is evident in the fact that the spectral features responsible are not visible in any way in the 10 ppm, 6 ppm, or 0.6 ppm emission spectra (top of Figure 24 and middle and bottom portions of Figure 25). They are indeed visible in the 60 ppm solution emission spectrum (top portion of Figure 25).
2. Closer observation of their relative distances in the spectrum suggests that they are originated by frequencies of about 120 Hz for the first couple of satellites and by a frequency range from 250 to 320 Hz for the other couple.

The first satellites as was discussed in Chapter 3 are quite likely due to 120 Hz electrical noise pick up in the moving mirror drive coil. The other two satellites are most likely due to modulation of the signal frequencies by the frequency of rotation of the plasma [74]. A further indication that the two satellites further from the major peaks are due to rotation of the plasma is obtained if we notice that these two satellites have broader width than the two others closer to the major peaks.

An interference noise such as the rotation frequency, being external to the spectrometer, has no phase

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Emission Spectrum



dependence with the frequency signal. Therefore it would generate broad satellites. On the other hand, a type of interference noise generated inside the spectrometer, such as a 120 Hz interference noise picked up in the moving drive mirror coil, would maintain some phase relationship in the signal frequency which ultimately translates to narrower satellites.

The signal-to-noise ratio spectrum shows a rather clean looking emission spectrum-like appearance. It suggests also some flicker noise limited character, i.e. even if the MgII 280.3 nm peak is about half the intensity of the MgII 279.6 nm peak their signal-to-noise ratio values are very close. In the emission spectrum of the 0.6 ppm solution of magnesium (bottom portion of Figure 25) a well defined background structure is revealed. Conspicuous also is the presence of the two carbon peaks at 193.1 nm and at 247.9 nm which are produced in the ICP source.

C. Peak Height Calibration Curve and Noise Behavior

Peak height intensities and peak height standard deviation values for the MgII 279.6 nm and the MgII 280.3 nm peaks as a function of the concentration of magnesium are plotted in Figure 26.

The plotted peak height intensities are background subtracted values obtained by subtracting from the actual

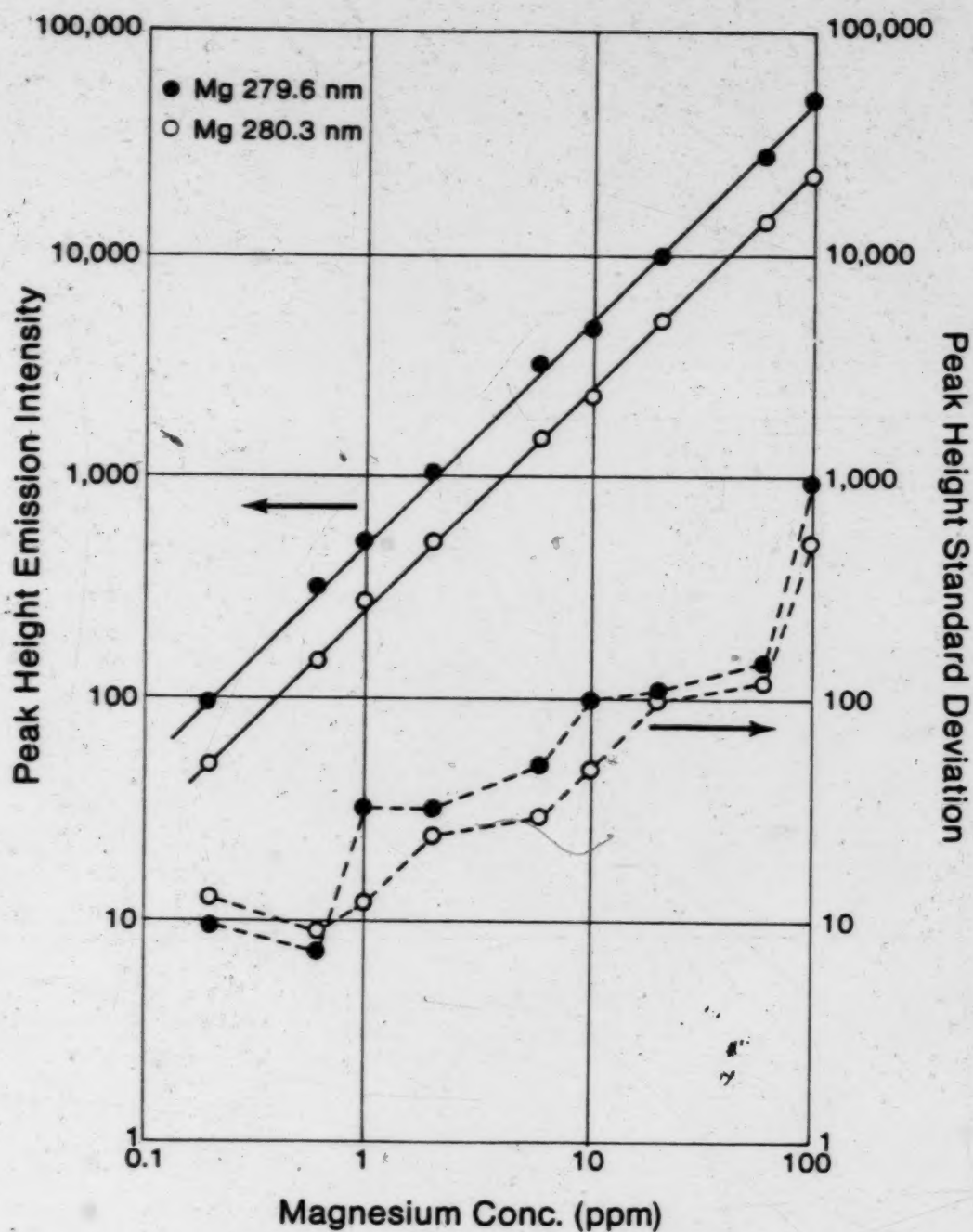


Figure 26. Plot of peak height emission intensity and peak height standard deviations as a function of the concentration of magnesium for the two major magnesium peaks.

peak height intensity the value of the background close to the pods of the peak. These background values are the result of careful examination of the spectral structure in the proximity of the peaks in the emission spectra at the various concentrations of analyte.

The plotted peak height standard deviation values are calculated by pooling the observed peak height standard deviation with the standard deviation at the background considered. The weighted least squares fitted [108,109] analytical calibration curves for the magnesium peaks are linear through all the concentration range considered with slopes of 0.996 for the MgII 279.6 nm peak and 0.998 for the MgII 280.3 nm peak. As the analyte concentration increases the peak height standard deviation and therefore the noise increases.

The slope of the increment of the standard deviation of the signal gives an indication of the nature of the limiting noise in the range of concentrations of analyte considered. This slope is equal to 0 for a background (or additive) noise limited situation, is equal to 0.5 for a photon shot noise (or transitive) [78] noise limited situation and finally equal to 1 for a flicker (or multiplicative) noise limited situation. The theoretical behavior of the signal standard deviation along with the corresponding behavior of the relative standard deviation

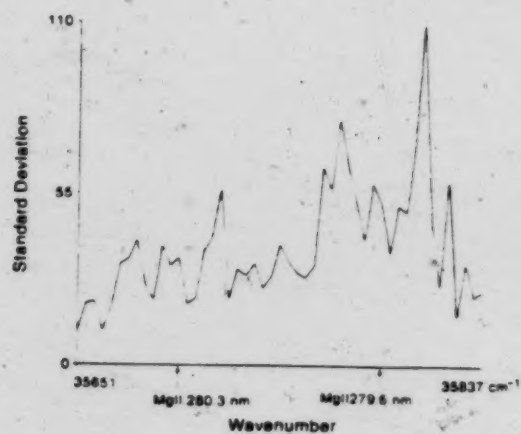
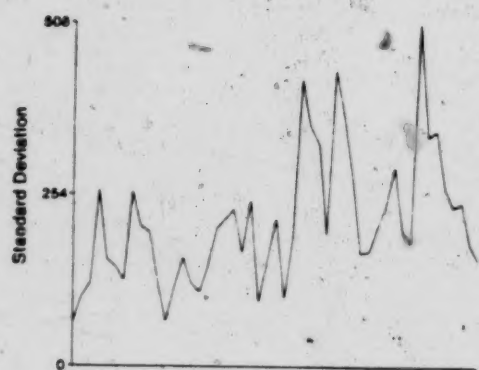
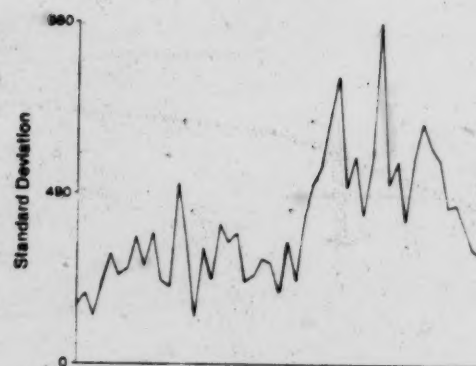
and signal-to-noise ratio are shown in Figure 4.

The experimental peak height standard deviation plots (Figure 26) are generally similar to the theoretical signal standard deviation behavior illustrated in Figure 4. A very interesting graphical representation of the noise behavior as a function of the concentration of analyte is shown in Figures 27 (a) and (b). In these figures the standard deviation and signal-to-noise ratio of the spectral region around the two major peaks are reported at various analyte concentrations. At low concentration (up to 1 ppm) the two peaks have signal-to-noise ratio values proportional to their relative signal intensity. This indicates a situation dictated by a constant value of noise (or detector noise limited). As we will see, it is more proper to call it a photon shot background noise limited situation. From 6 ppm and up, nearly the same signal-to-noise ratio value for both peaks is observed. This strongly suggests a flicker noise limited situation.

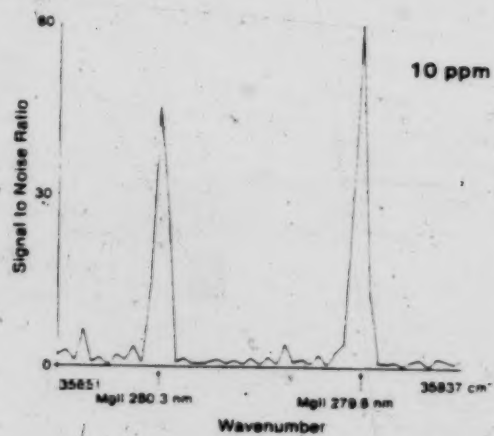
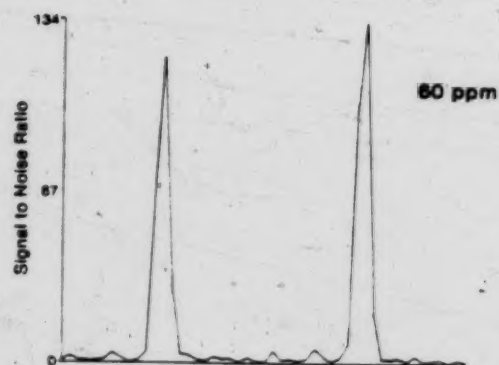
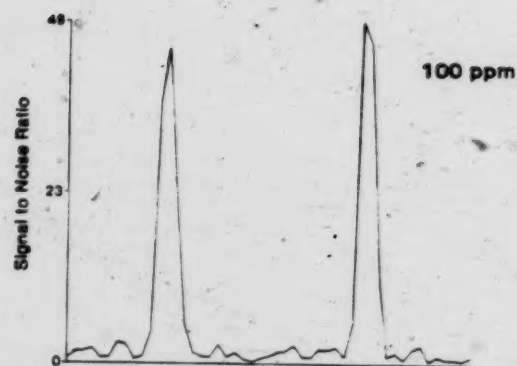
This detailed kind of information that is easily observed with this type of spectral statistical representation is rather remarkable if we think that it cannot be easily obtained in conventional spectroscopy where typically the statistics are calculated at single points in the spectrum. In our case the statistics have

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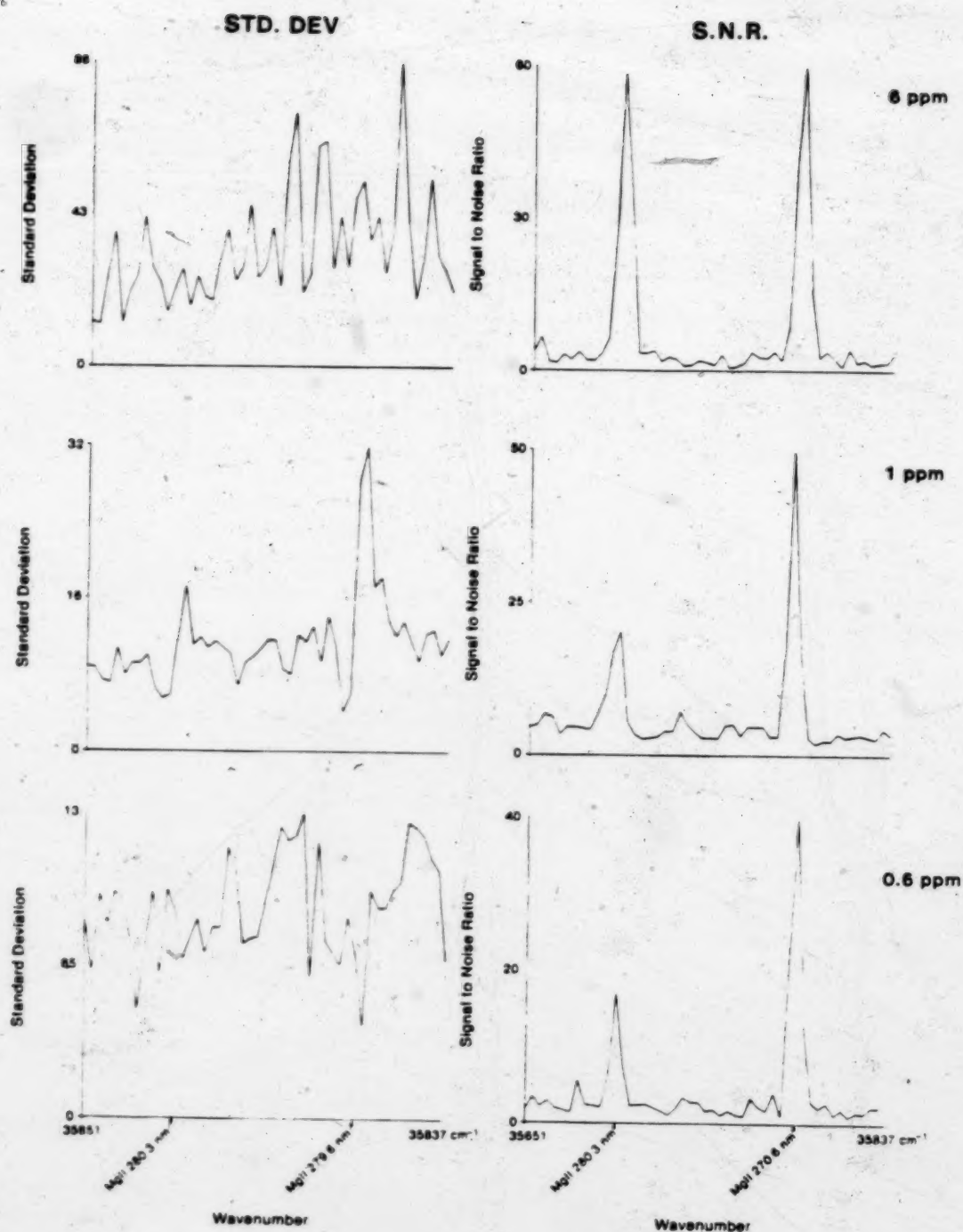
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been expanded to the level of the whole spectrum and therefore a more complete picture of the functional dependence of the noise on the signal level is available and more information about the experimental conditions can be obtained.

At the concentration of 60 ppm a jump is quickly noticed for both peaks. From the value of about 60 the signal-to-noise ratio at the peaks increased to a value of about 130. Even if we are momentarily left to speculate about the reason for this sudden behavior, the fact that the two peaks behave in a very similar fashion suggests that we still are in a flicker noise limited situation. The explanation of the occurrence of such a jump in spectral quality can be found by examining the standard deviation spectrum at the same concentration. Even if the noise is generally speaking, peak localized, like at the other analyte concentrations, we notice that the standard deviation at the exact peak top is unusually low for both peaks. This type of behavior is further proof of the fact that the spectral noise observed is determined by experimental bias error rather than random statistics. For a complete discussion of this point refer to Chapter 3.III.D.

The decrease of the signal-to-noise ratio peak values at 100 ppm corresponds to a negative slope of the signal

standard deviation. This type of disturbance, which can be called non-linear noise or long term drift, corresponds to larger relative increase in the noise than in the signal which eventually may lead to a disruption of the linearity of the calibration analytical curve. Whether this is what really happens in our case could not be proven because in order to test this hypothesis we would have had to change the electronic gain setting to accommodate higher concentrations than 100 ppm. At these new experimental conditions, a 10 ppm solution cannot be properly used as a standard. The change of experimental conditions would make the comparison of the noise behavior at different analyte concentrations a very arduous task.

Since a great deal of variation in the noise distribution is observed at the various magnesium concentrations a different signal emission intensity parameter other than the peak height has been considered.

D. Peak Area Calibration Curve and Noise Behavior

The peak area values plotted as a function of the concentration of magnesium in Figure 28 were calculated using the trapezoidal rule [110], i.e. by summing the values of the emission intensity of the points immediately close to the central peak point on both sides and adding half emission intensity value of the initial and final point. The number of points for each peak has been chosen

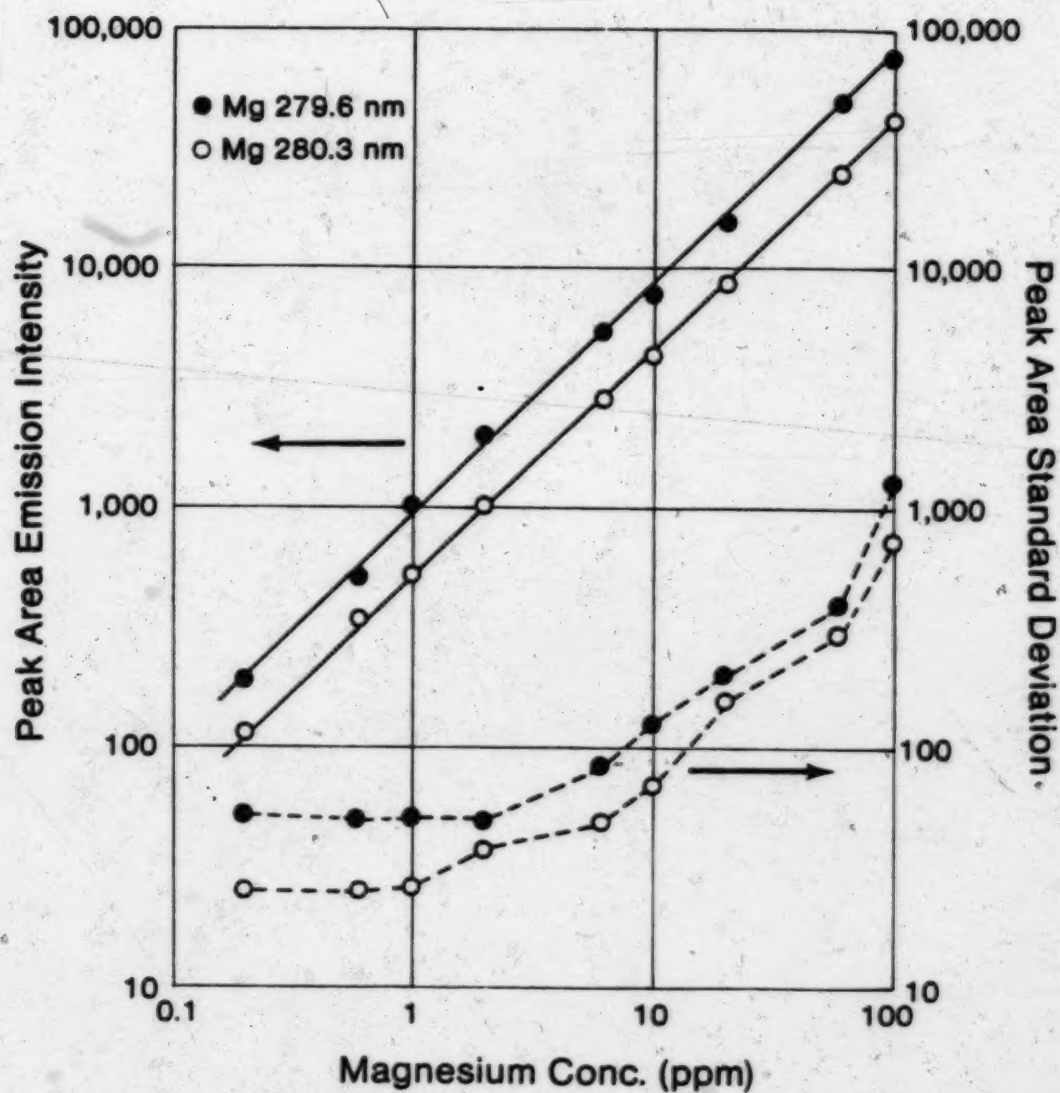


Figure 28. Plot of peak area emission intensity and peak area standard deviation as a function of the magnesium concentration for the two major magnesium peaks.

so that the calculated pooled standard deviation has a minimum value. This number has been found to be a total of 7 points. The weighted least squares fitted peak area calibration curves of the major magnesium peaks have a slightly lower linearity (slopes of values 0.994 for the MgII 279.6 nm peak and 0.985 for the MgII 280.2 nm peak) than the corresponding peak height calibration curves. On the other hand, the plots of the peak area standard deviation as a function of the concentration of analyte indicate a less scattered behavior at low concentrations of analyte than the corresponding peak height standard deviation plots (Figure 26). This smoother aspect is reflected in the behavior of the plots of the peak area signal-to-noise ratio as a function of the concentration in Figure 29. This plot seems to indicate a trend closer to the theoretical one (Figure 4) than the corresponding plot for the peak heights (Figure 30).

In the next section a mathematical treatment for identifying the limiting noise along a calibration curve, when statistical data are available, will be discussed.

V. Mathematical Analysis of Limiting Noise

As it has been previously pointed out if only one type of noise is responsible for the noise observed, finding the limiting noise is simply a matter of observing the slope of the plot of the signal fluctuation as a

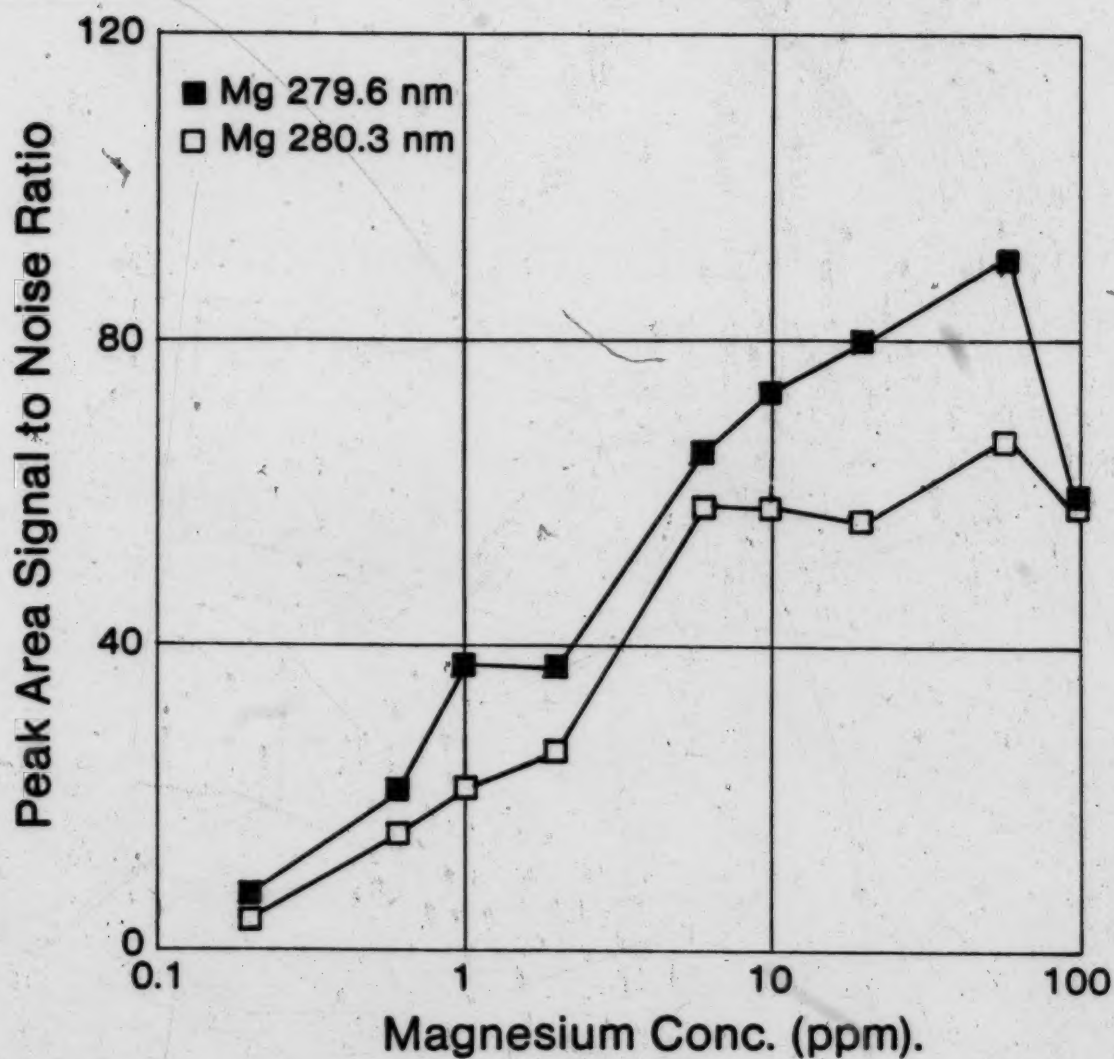


Figure 29. Plot of peak area signal-to-noise ratio as a function of the concentration of magnesium for the two major magnesium peaks.

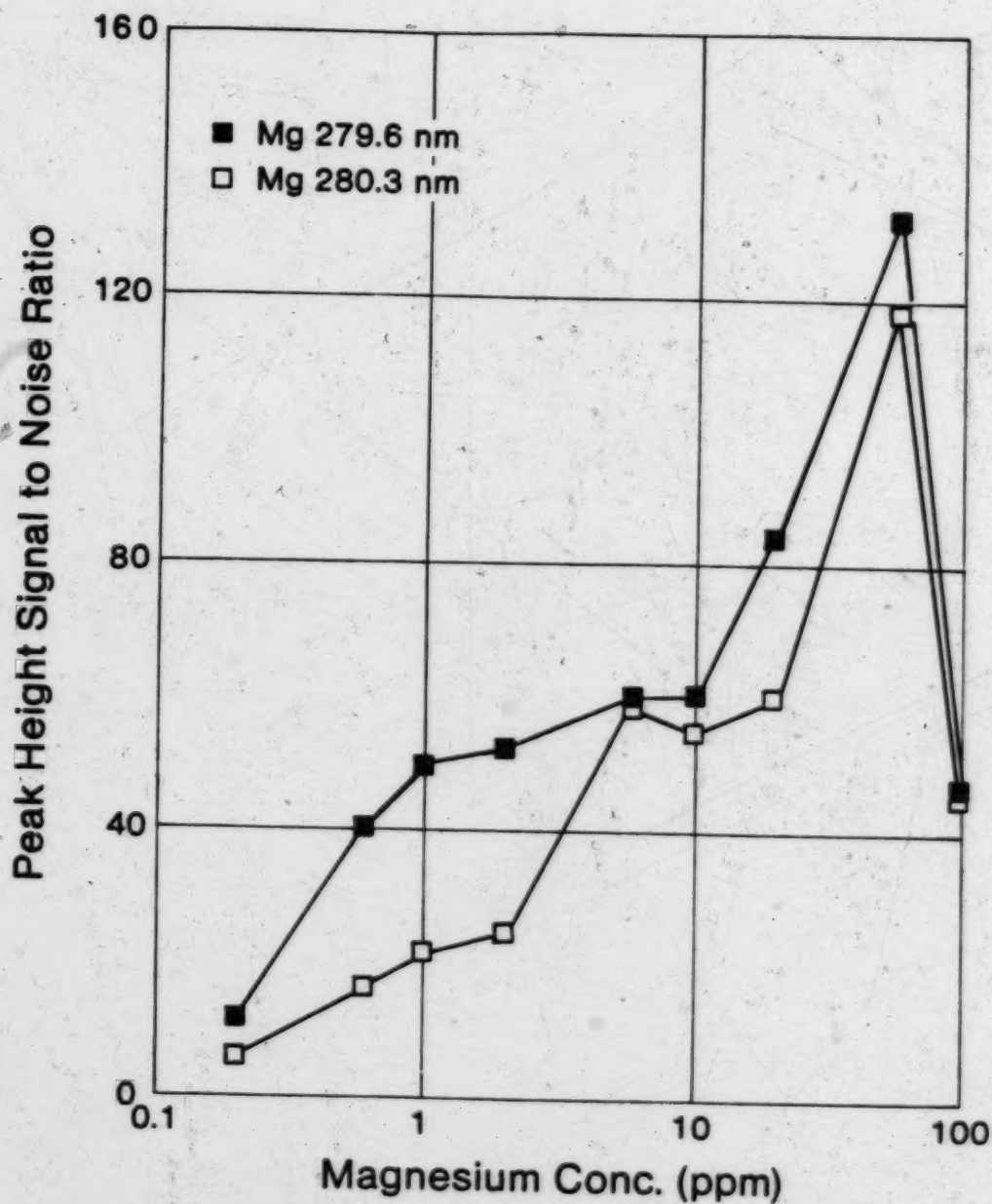


Figure 30. Plot of peak height signal-to-noise ratio as a function of the concentration of magnesium of the two major magnesium peaks.

function of the analyte signal intensity. The problem is more complex in the actual experimental situation where typically more than one type of noise contributes simultaneously to the total observed noise.

In this section a simple mathematical analysis of the limiting noise in practical atomic emission analysis is proposed. In this analysis the absolute independence among the different kinds of noise is assumed. In such a situation the signal variances sum up linearly and the total observed variance is due to three separate contributions in terms of background, photon shot noise and flicker noise. Therefore the following mathematical equation for the total observed variance is valid:

$$V = a + bx + cx^2 \quad (16)$$

where V is equal to the total observed variance, x is equal to the signal value, and a , b , and c are equal to the coefficients for the background, photon shot and flicker noise.

If a sufficient number of signals and signal variance values are available, the problem of finding the relative contributions of the different types of noise to the total noise corresponds to finding the values of the coefficients a , b and c . These coefficients can be easily

calculated through a polynomial least square fitting procedure [111]. The procedure was tried over the peak area experimental data of magnesium reported in Figure 28. Although conclusive results could not be obtained, due to the limited number of data points available with slope higher than zero, preliminary calculations show a higher contribution of the flicker noise than the photon shot noise to the total observed noise in the concentration range between 1 and 10 ppm. Visual observation and calculations allow the identification of the concentration range from 0.2 to 1-2 ppm as being prevalently background noise limited and the concentration range from about 6-10 ppm to 100 ppm as being chiefly flicker noise limited.

These preliminary results seem to indicate that at the experimental conditions considered, the range of concentration of existence of the photon shot noise limited situation is very small, if it exists at all.

F. Background Noise Behavior Comparison to Peak Noise Behavior

The background and the background standard deviation in two background spectral regions as a function of the concentration of analyte are plotted in Figure 31. The two chosen spectral background regions meet these requirements:

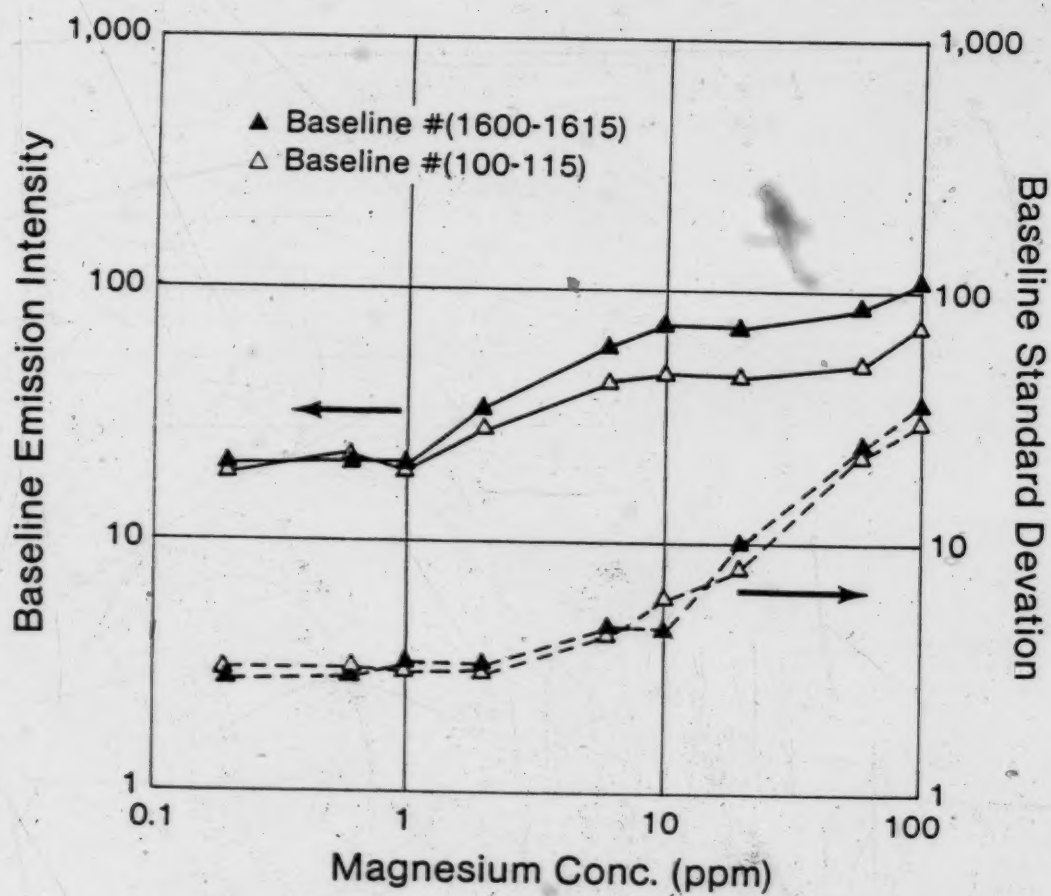


Figure 31. Plot of baseline intensity and baseline standard deviation in two background regions as a function of the concentration of magnesium.

1. They are free of spurious spectral features.
2. They are not on sloping spectral regions.
3. They are not very close to spectral regions where peaks belonging to zinc, iron and manganese fall.

(These elements are added to magnesium in a further study that will be described in Chapter 5.)

The standard deviation background values plotted are calculated pooled standard deviation values of 8 alternate points in the spectral regions including the points 100 and 115 for the first background region and 1600 and 1615 for the second one. Eight was chosen as the number of points for the background to obtain a more strict analogy with the seven points used to define the peak area. Since the background regions considered are far from the two major analyte peaks in the emission spectrum, no highly noticeable differences are observed in the noise behavior of the two background regions. The standard deviation values increase with the analyte concentration. This strongly suggests the presence of a multiplex disadvantage effect.

In order to gain some insight on the actual repartition of the total noise between the background and the peak spectral locations at the various analyte concentrations, the average standard deviation values for the two background regions and the two major magnesium

peaks as a function of the concentration of analyte are plotted in the same graph (Figure 32). The peak area standard deviation values are about 20 to 60 times higher than the corresponding background values. If we divide the total analyte concentration range in three portions where we observe a visual change in slope we can distinguish 3 zones: from 0.2 ppm to 1 ppm, from 1 ppm to 6-10 ppm and from 6-10 ppm to 100 ppm of analyte concentration. The calculated slopes in these three zones for the plot of the average standard deviation of the two peak areas of the analyte and the average standard deviation of the two background regions are given in Table 6. Narrow lines with one arrow indicate a theoretical photon shot noise limited behavior (slope = 0.5); narrow lines with two arrows indicate a theoretical flicker noise limited behavior (slope = 1.0).

In the region from 6-10 to 100 ppm of analyte concentration the noise on the peaks increases directly as the signal level (slope = 1.02) whereas the noise in the background increases at a lower rate (slope = 0.80). In the region from 1 to 6-10 ppm of analyte concentration both rates of increase of noise for the peaks and the background are lower than the rate of increase in an analyte photon shot noise limited situation (slope = 0.5). For the noise on peaks the calculated slope is 0.38

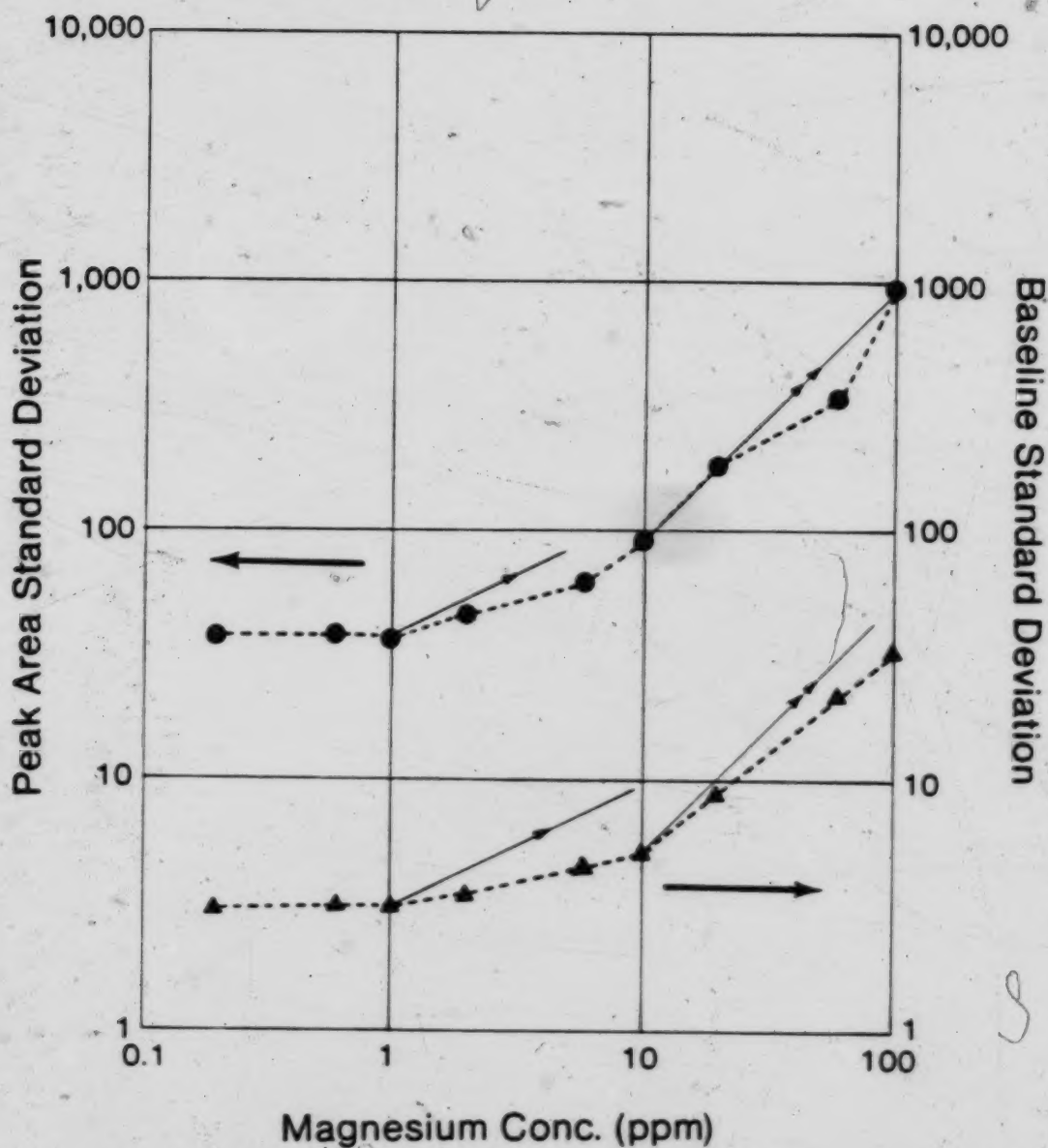


Figure 32. Plot of peak area standard deviation and baseline standard deviation as a function of magnesium concentration.

Table 6
Calculated Slopes of Plots of Standard Deviation Values

ppm	Slope		
	0.2-1 ppm	1-6(10) ppm	6(10)-100
Average standard deviation of peak areas	0	0.38	1.02
Average standard deviation of background regions	0	0.19	0.80

whereas for the background it is 0.19.

These results show that consistently a higher amount of noise concentrates at the peaks rather than in the background all along the calibration curve.

G. Interferogram and Spectrum Root Mean Square Value

A more universal picture of the noise behavior can be obtained if instead of considering the analyte peaks as the signal values we consider the root mean square value of the total signal. The rationale behind this is that in Fourier spectroscopy all spectra are observed at once, and the noise observed in practical experimental conditions with a photomultiplier detector is quadratically or linearly proportional to the total original light. The root mean square (RMS) value represents the concentration in one single value of the total light power hitting the detector. The calculated RMS values for the interferograms are plotted as a function of concentration of magnesium in Figure 33.

The calculated RMS values for the spectra are also reported in the same figure. It is interesting to notice the perfect parallelism of behavior between the two RMS plots. This result can be considered as the experimental proof of the validity of Rayleigh's theorem [112] (derived from Parseval's theorem for Fourier series) which states: "The integral of the squared modulus of a

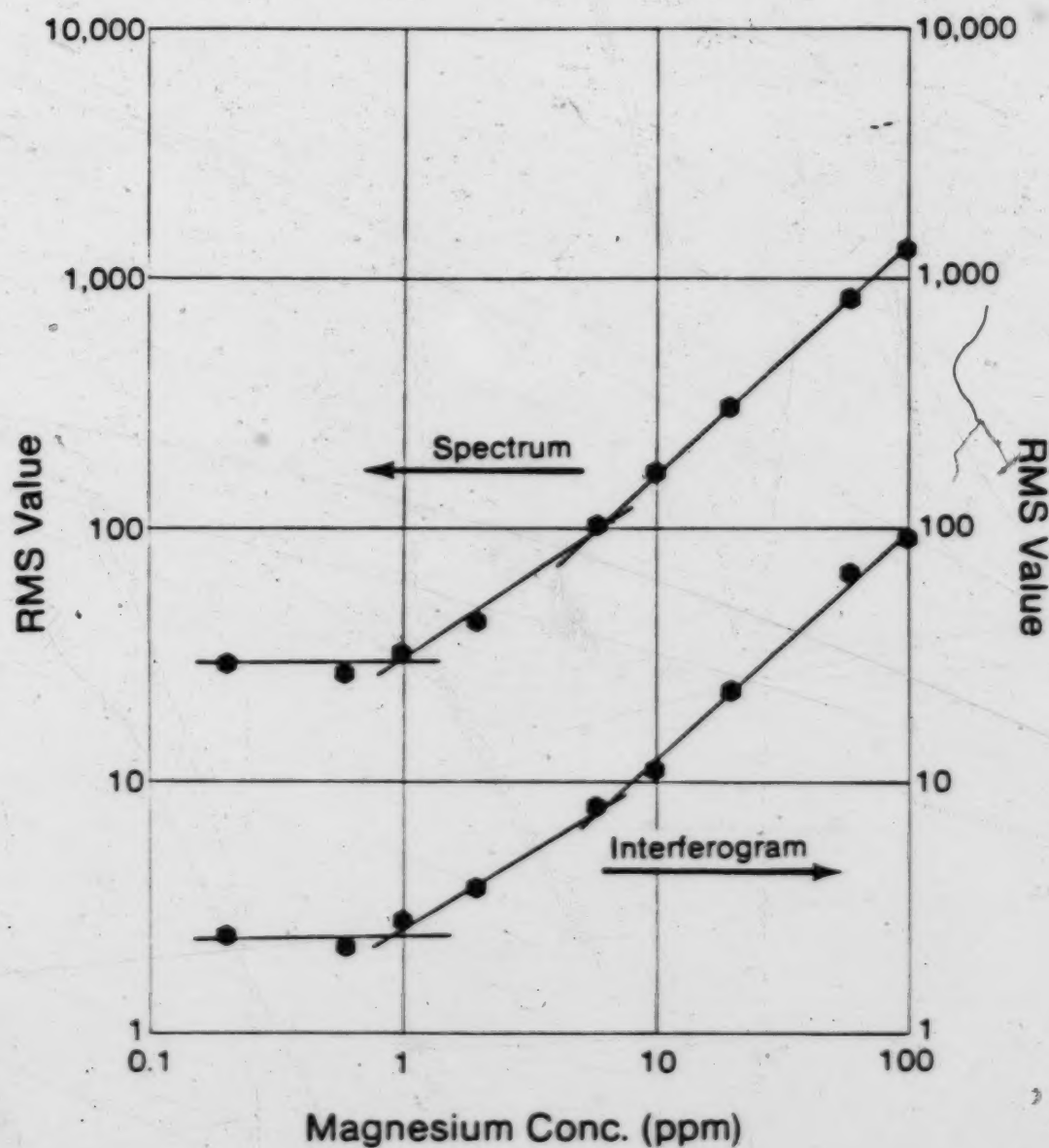


Figure 33. Plot of interferogram and spectrum root means square (RMS) value as a function of the magnesium concentration.

function is equal to the integral of the squared modulus of its spectrum."

The point to be stressed here is that by using the RMS value taken as the representation of the signal, the noise behavior can be tackled from a different standpoint. In Table 7 the calculated slopes for the plots of the RMS values as a function of the concentration of analyte are listed for the three portions of concentration ranges that have a different slope. These 3 regions are: from 0.2 to 1 ppm, from 1 ppm to 6 ppm and from 6 ppm to 100 ppm of analyte.

The following major observations can be made:

1. The slopes of the RMS values plot for the interferogram and spectrum are the same for the same concentration range considered.
2. The effective signal hitting the detector in the region from 0.2 to 1 ppm analyte concentration does not increase. The RMS values remain virtually constant. The total signal registered at the detector is mainly due to the level of background present.
3. The slope of the RMS value plot in the region from 6 to 100 ppm of analyte concentration, being mainly determined by the signal analyte peaks is 0.89.
4. The slope of the RMS values plot in the region between 1 to 6 ppm of analyte concentration, being determined

Table 7
Calculated Slopes of Plots of RMS Values

	Slope		
	0.2-1 ppm	1-6 ppm	6-100 ppm
RMS Interferogram	0	0.56	0.89
RMS Spectrum	0	0.56	0.89

by the contribution of both background, and signal analyte peaks, is 0.56.

If we consider the RMS as the parameter indicating the signal value and we compare with the calculated results for the noise at the peaks and in the background (Table 6) we can notice that: (a) the noise on the peak has a higher rate of change (slope = 1.02) than the total signal itself or RMS value (slope = 0.89) in the region between 6 and 100 ppm in analyte concentration. In the same region the noise at the background increases at a lower rate (slope = 0.80). This corresponds to a rate of noise change higher than a flicker noise regime for the peak noise and lower than a flicker noise regime for the background noise. (b) In the region from 1 to 6 ppm of analyte concentration the RMS values increase with a slope of 0.56 whereas the noise at the peak increases with a slope of 0.38 and the noise in the background with a slope of 0.19. Again the peak noise seems to concentrate in itself the largest portion of the noise. In this respect, it is interesting to notice that a photon shot noise limited situation would predict a rate of increase of noise equal to a slope of 0.28.

We can finally summarize the noise behavior observed in these main points:

1. The noise at the background is consistently lower than

at the peaks.

2. In the concentration region from 0.2 ppm to 1 ppm of analyte we most likely observed a background photon shot noise limited situation.
3. The concentration region from 6 to 100 ppm most likely renders the experimental conditions flicker noise limited.
4. Doubts still persist in the identification of the noise regime in the analyte concentration region ranging from 1 to 6 ppm. It could be photon-shot noise limited or a combination of a background and flicker noise limited situation.

H. Comments

The conclusions about the identification of the various noise regimes along the analyte calibration curve were reached by treating the analyte peaks as in classical dispersive atomic spectroscopy.

The extrapolation of this noise behavior to the one found in Fourier spectrometry at times is not justified. Let's consider for instance the flicker noise regime.

In dispersive atomic spectroscopy considering the same analysis time the precision (S.N.R. value) at the analyte peak remains unchanged when the analyte emission increases.

In Fourier spectrometry in flicker noise regime,

expression 11 was derived in the introductory chapter for the signal-to-noise ratio for any spectral feature of intensity I .

According to this theoretical equation the signal-to-noise ratio of a spectral peak of intensity I is directly proportional to its intensity I and the square root of the analysis time and inversely proportional to the total intensity of the spectrum. If the same analysis time is spent for each datum on the calibration curve, as is the case in the experimental results for the magnesium calibration curve, the signal-to-noise ratio expression reduces to the following form:

$$(S.N.R.)_{FT} \propto \frac{I}{I_{total}} \quad (17)$$

If the calculated RMS values of the analyte peak and the total spectrum at the various analyte concentrations are substituted in the expression, in principle, information about the concentration range in which the analyte is flicker noise limited can be obtained.

In practice, this procedure confirmed what we already knew about the concentration range between 6 and 100 ppm of magnesium. That is, the latter concentration range is largely flicker noise limited. The total RMS spectral value in this region is 0.89 (Table 7) and this value,

which can be attributed to the analyte peak RMS value, is close to the slope of the noise in the same region, consistently about 1 (Figures 26, 28 and 32).

When the same procedure was tried on the range of concentration between 1 and 6 ppm of analyte, unsatisfactory correlations were found, the probable reasons being: (1) at the concentration range considered the analyte peak makes up an insignificant portion of the total signal and (2) at the experimental conditions the reproducibility of the background shape is rather poor.

Although this procedure did not fulfil our expectations, the exercise was not useless because it showed us the validity of the RMS parameters as diagnostic tools for studying noise in FTS. In fact, the substitution in equation 17 of RMS values, when they can be calculated with sufficient precision, allows the study of analyte precision to be made without carrying out statistical time consuming procedures. This can be considered quite a remarkable advantage of the technique of ICP-FTS.

IV. Zinc Internal Standard Study

A. Introduction

The magnesium quantitative study was carried out by meticulously monitoring and controlling interferogram shape and symmetry of the analyte at different concentrations and by using a 10 ppm solution of magnesium as a standard according to the procedure outlined in Chapter 3. This strict and continuous control of the experimental conditions allowed us to achieve a high level of information of a fundamental nature about the noise behavior in ICP-FTS atomic emission analysis. In the zinc study, on the other hand, in order to test the applicability of internal standardization as a signal-to-noise enhancement technique, the controlling procedures used in the case of the magnesium study were not carried out.

B. Experimental Conditions

Solutions containing 1, 2, 6, 10, 20, 60, 100, and 200 ppm of zinc added to 10 ppm of cadmium were aspirated into the ICP. The solar blind photomultiplier tube was operated at the potential of 660 V. The gain setting was 10^6 , the filtering conditions were from 10.0 to 21.5 kHz. The data acquisition and treatment were carried out in exactly the same fashion as the magnesium quantitative study.

C. Emission, Standard Deviation and Signal-to-Noise Ratio Spectra

The emission spectrum and the emission, standard deviation, and signal-to-noise ratio spectra for the solution containing 1 ppm of zinc and 10 ppm of cadmium as internal standard are shown in Figures 34 and 35. The usual 3-character set labeling code for the horizontal axis is used in the emission spectrum in Figure 34. This spectrum is dominated by a well defined background which makes up the largest portion of the signal power.

A rather peculiar behavior is now noticed in the standard deviation spectrum (middle portion of Figure 35). The noise, instead of being localized on the peaks, as we have seen in all reported results so far, follows the background structure. This is again a strong indication that the noise distribution along the wavenumber axis is dictated by multiplicative factors. In this case most of the signal that can modulate a spurious frequency in the various ways we described in Chapters 3 and 4 resides in the background.

In this respect it should be added that the same kind of noise behavior is observed at a low concentration of magnesium in the study reported in the first part of this chapter (these results are not shown). The signal-to-noise ratio spectrum shows the usual clean looking emission spectrum form (bottom portion of Figure 35).

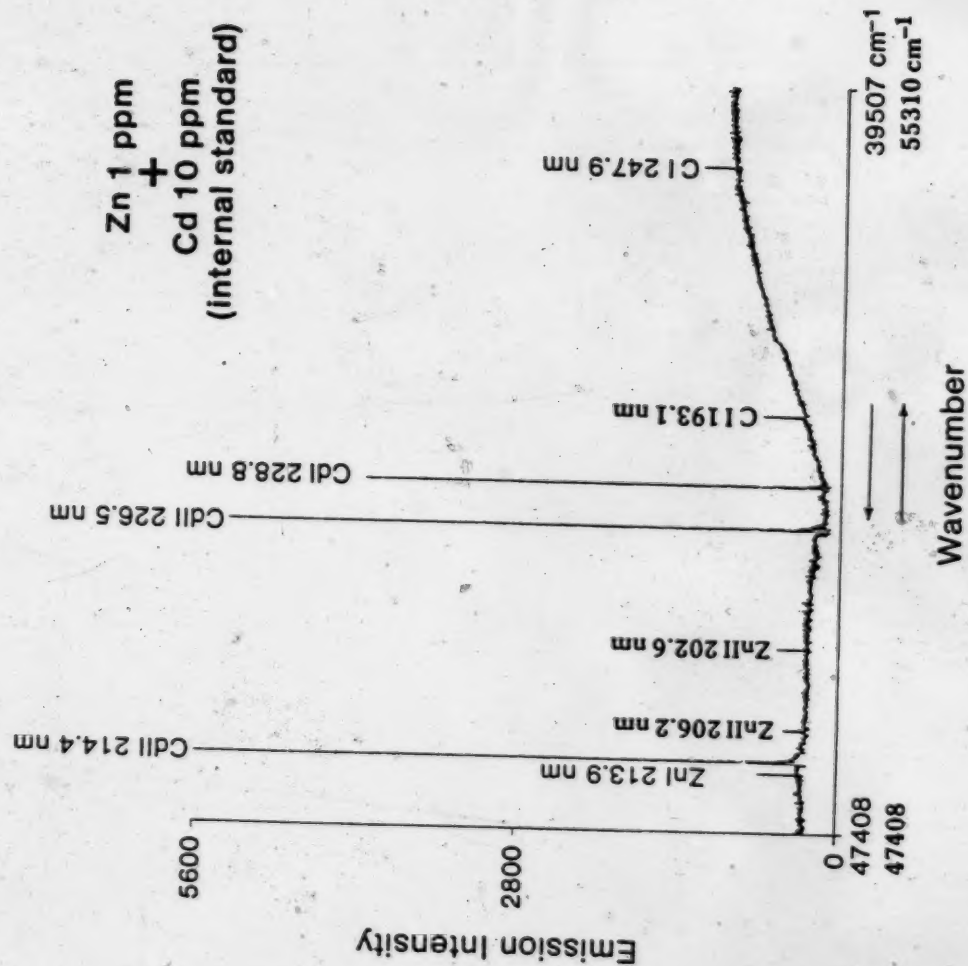
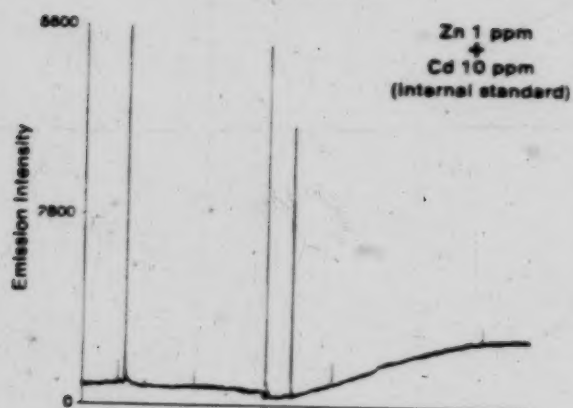


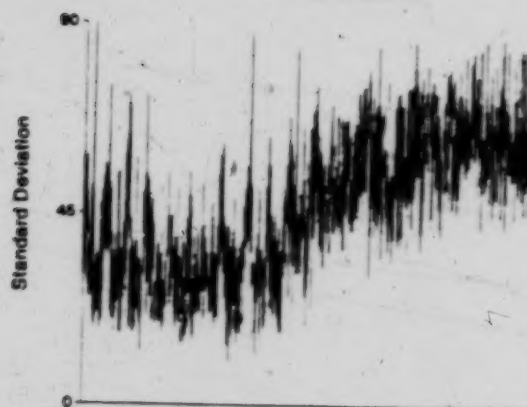
Figure 34. Emission spectrum of a solution containing 1 ppm of zinc and 10 ppm of cadmium (internal standard) in the ultraviolet spectral region.

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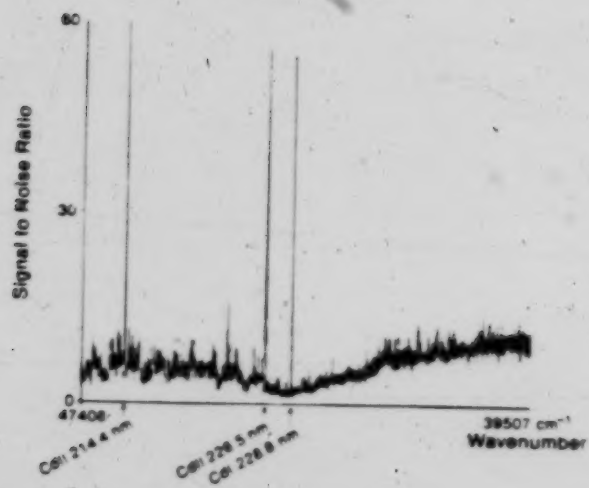
Emission Spectrum



STD. DEV. Spectrum



S.N.R. Spectrum



The emission spectrum and the emission, standard deviation and signal-to-noise ratio spectra for the solution containing 400 ppm of zinc and 10 ppm of cadmium as internal standard are shown in Figures 36 and 37. In this case the peaks make up a large part of the total signal power therefore spectral and noise behaviors are similar to the ones reported in the study of magnesium.

A great number of satellites appear in the emission spectrum. This presence can easily be explained if we think that each peak produces two sets of satellites (4 in total) and 3 major peaks are present.

The standard deviation spectrum as usual parallels this behavior by showing a large number of satellites. The signal-to-noise ratio has the usual emission spectrum form.

D. Internal Standard Technique and Correlation Coefficient

The technique of internal standardization consists in taking as the parameter for the analyte signal the ratio between the analyte emission intensity and the emission intensity of an element other than the analyte chosen as the internal standard. The efficacy of the technique as a precision enhancement method resides in the assumption that external fluctuations affect in the same exact manner the analyte and internal standard emission intensities.

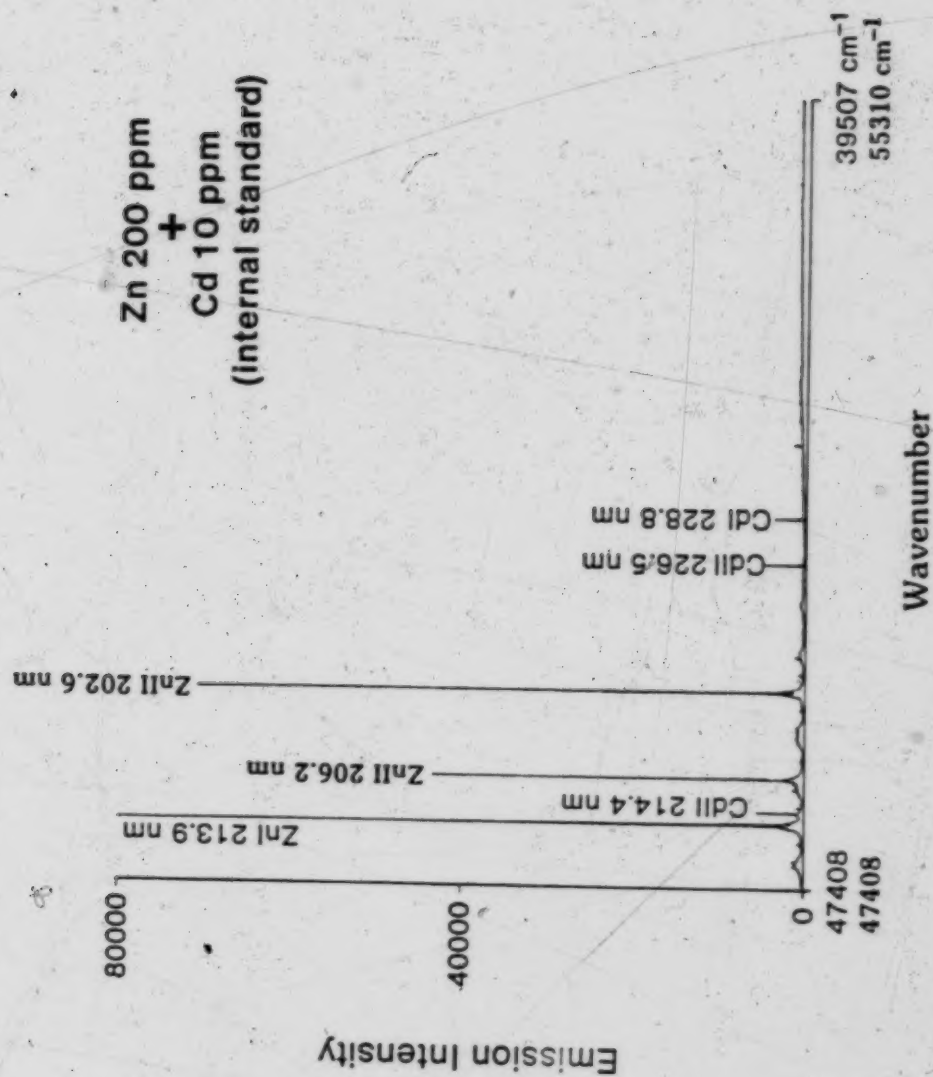
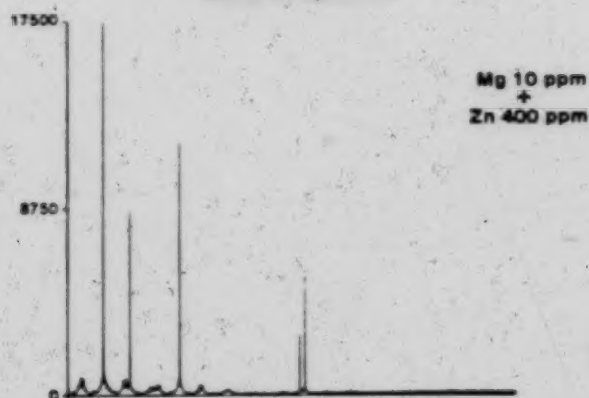
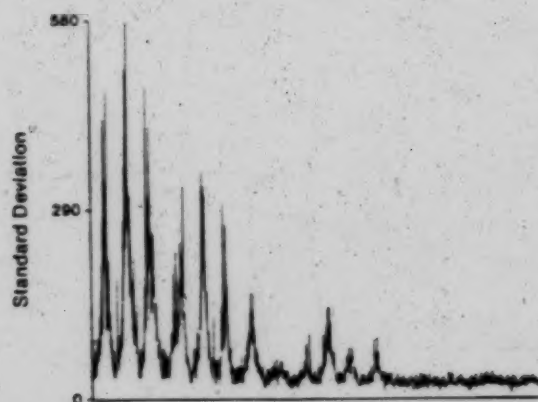


Figure 36. Emission spectrum of a solution containing 200 ppm of zinc and 10 ppm of cadmium (internal standard) in the ultraviolet spectral region.

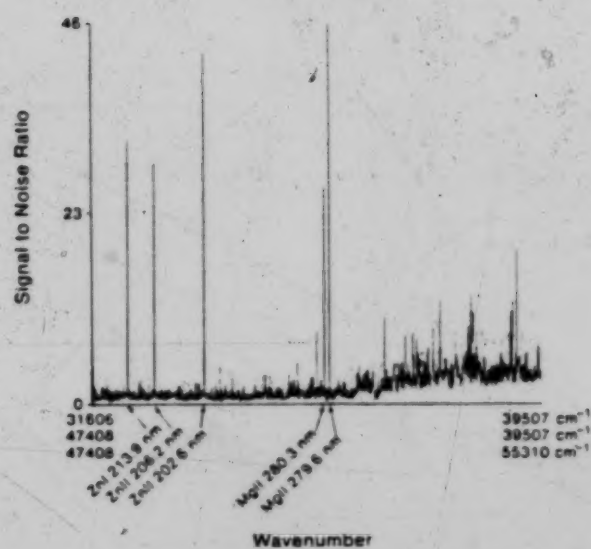
Emission Spectrum



STD. DEV. Spectrum



S.N.R. Spectrum



From what has just been said it is evident that Simultaneous measurement, in addition to similarity of behavior of fundamental parameters such as ionization and excitation energies, atomic weight, etc. is one of the major requirements for obtaining the maximum efficacy from the internal standardization technique. Simultaneous measurement capability is one of the trademarks of Fourier spectroscopy therefore it seemed appropriate to try internal standardization with our system.

A mathematical method to check the parallelism of variation between the analyte peak intensity and the internal standard is provided by the calculation of the correlation coefficient of a statistical set of data at each concentration by using the following formula [108,113].

$$r = \frac{\text{COVAR}_{xy}}{\text{S.D.}_x \text{ S.D.}_y} \quad (18)$$

where r is equal to the correlation coefficient, x indicates the analyte emission intensity, y indicates the internal standard emission intensity, S.D._x is equal to the standard deviation of the analyte emission intensity, S.D._y is equal to the standard deviation of the internal standard emission intensity, and COVAR_{xy} is equal to the covariance between the analyte peak height and the internal standard peak height.

COVAR_{xy} is calculated according to the equation [12,13]:

$$\text{COVAR}_{xy} = \frac{\sum xy - (\sum x \sum y / n)}{n-1} \quad (19)$$

where n is equal to the number of runs for each concentration of analyte, i.e. 8 in our case.

A visual representation of the concepts just outlined is presented in Figures 38 and 39. In these two figures the peak height emission intensities of two different solutions for the CdII 214.4 nm peak (internal standard) and the three major zinc peaks as a function of the run number are plotted. From a visual observation of these two figures it is evident that the behavior shown in Figure 39 is best suited to internal standardization. This fact is also reflected in the calculated correlation coefficients ranging between 0.96 and 0.98. On the other hand the dissimilarity of behavior shown in Figure 38 is apparent from the poor correlation values that in some cases are negative.

E. Signal-to-Noise Ratio Plot

The noise in the ratio of the emission signals (S.D._{x/y}) can be calculated at each data point with the following equation [12,13]:

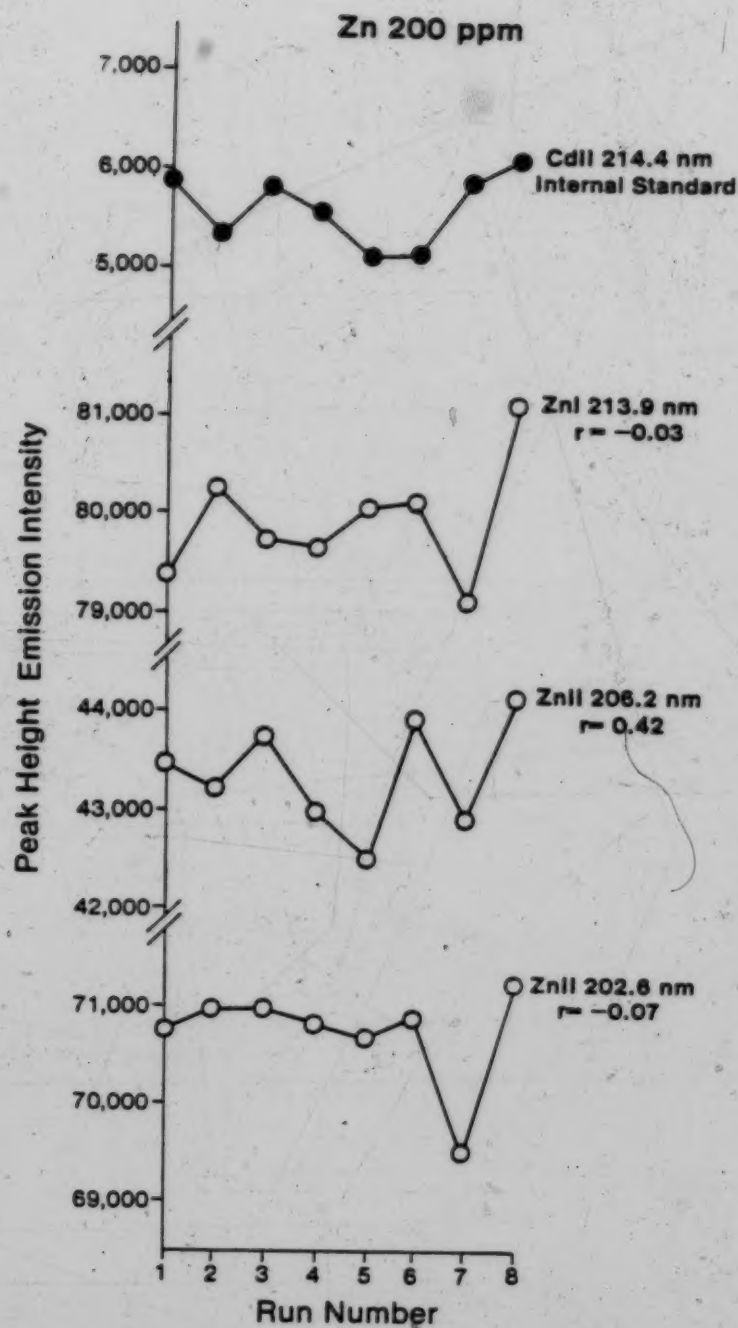


Figure 38. Peak height emission intensity as a function of the run number for the internal standard peak and the three major zinc peaks of a solution containing 200 ppm of zinc and 10 ppm of cadmium.

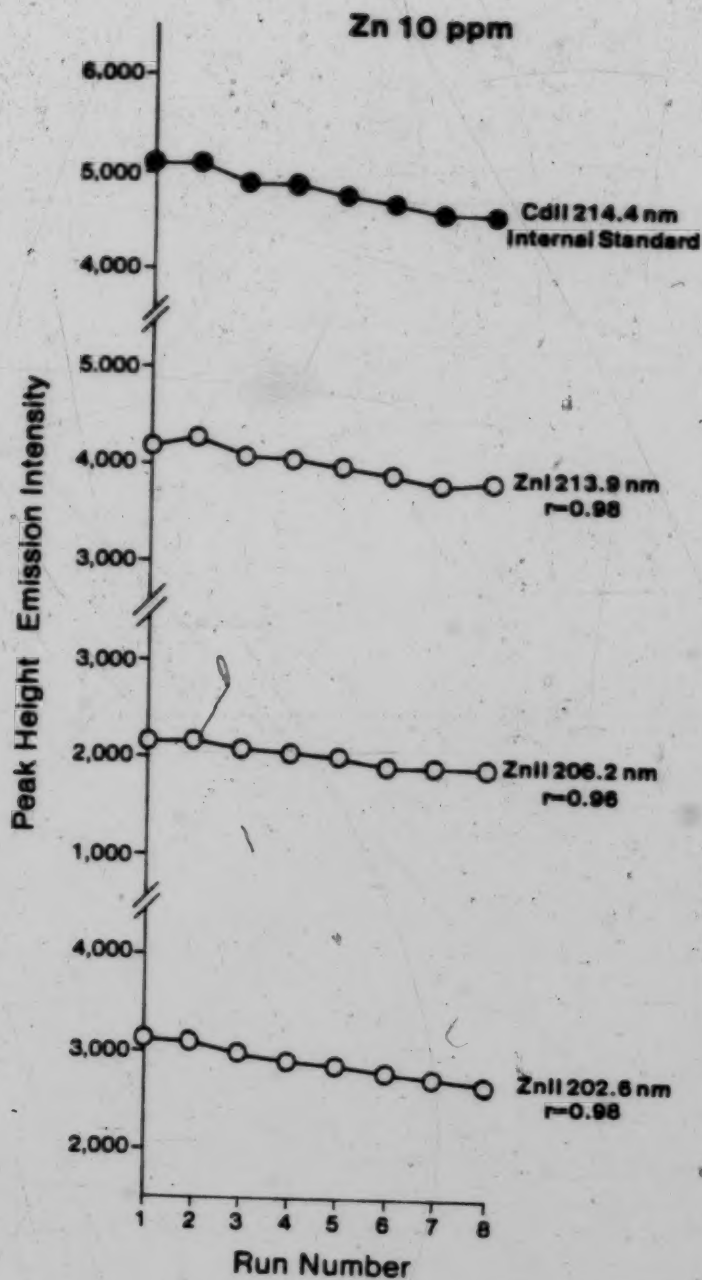


Figure 39. Peak height emission intensity as a function of the run number for the internal standard peak and the three major zinc peaks of a solution containing 10 ppm of zinc and 10 ppm of cadmium.

$$S.D._{x/y} = \sqrt{\left(\frac{\bar{x}}{\bar{y}}\right)^2 \times \left[\left(\frac{S.D._x}{\bar{x}}\right)^2 + \left(\frac{S.D._y}{\bar{y}}\right)^2 - 2r \frac{S.D._x S.D._y}{\bar{x}\bar{y}}\right]} \quad (20)$$

where $\bar{x}/\bar{y}$ is the ratio of the averages of the intensities of the analyte over the internal standard. The signal-to-noise ratios calculated at various concentrations for the ZnI 213.6 nm peak, according to the general expression

$$(S.N.R.)_{x/y} = \frac{\frac{\bar{x}}{\bar{y}}}{S.D._{x/y}} \quad (21)$$

are shown in Figure 40. For comparison the signal-to-noise ratio plot is shown when no internal standard is used for the same peak.

In the concentration region ranging from 6 to 60 ppm a signal-to-noise ratio enhancement is noticed in the case where the internal standard was used. At lower concentrations the signal-to-noise ratio remains almost unchanged. A dramatic reversal of behavior is noticed at the concentration of 200 ppm of Zn where the use of the internal standard causes a sudden decrease in signal-to-noise ratio value. This behavior could have been predicted on the basis of the calculated correlation coefficient.

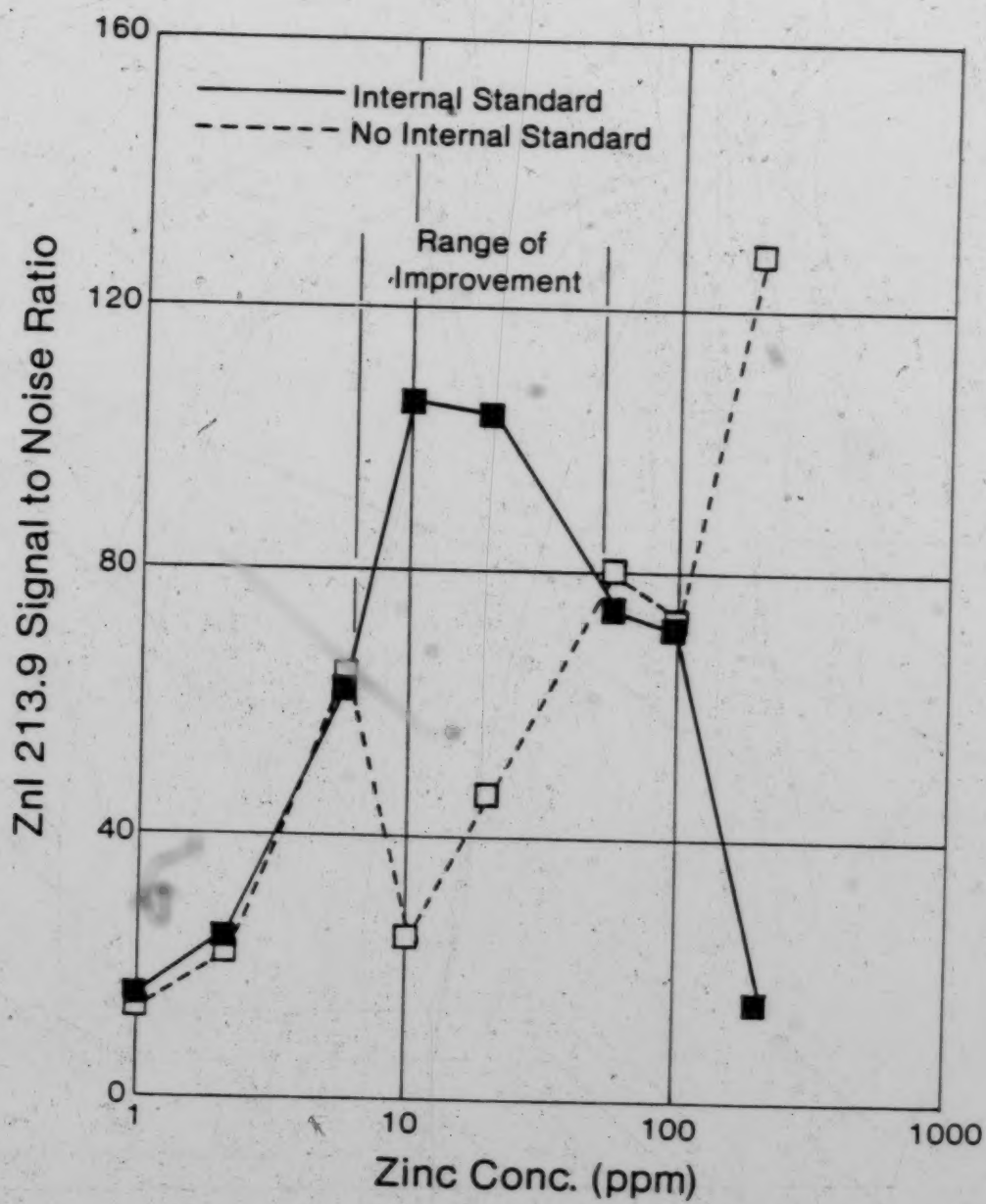


Figure 40. Plot of ZnI 213.9 nm signal-to-noise ratio as a function of the concentration of zinc with and without internal standard.

V. Conclusions

From the study described in this chapter the following major conclusions can be made.

1. Noise is distributed in the emission spectra in two main ways: (a) when the analyte signal is small relative to the total power the noise distribution is quite uniform and its value parallels the background, (b) at higher analyte concentrations noise is localized on peak features.
2. Electrical noise pick up and rotation of the plasma are the major factors determining the presence of spurious spectral features in the emission spectrum and anomalously noisy regions in the standard deviation spectrum.
3. At the experimental conditions considered, the study of magnesium shows that (a) the concentration range from 6 to 100 ppm of analyte can be referred as a flicker noise limited situation, (b) the concentration range from 0.2 to 1 ppm of analyte can be referred as a background photon shot noise limited situation, (c) the concentration range from 1 to 6 ppm of analyte can be an analyte photon shot noise limited situation or a situation dominated by background and flicker noise.
4. The fact that the background standard deviation increases with an increase of the concentration of

analyte suggests the presence of a multiplex disadvantage effect.

5. Overall, RMS values are useful parameters to be used in noise studies of ICP-FTS. Well behaved experimental situations can lead to the study of the noise without the need for statistical data to be collected.
6. Internal standardization is somewhat effective in enhancing the precision of the analyte signal. To obtain the maximum efficiency from the method it is important to match the peak intensities of the internal standard and analyte.
7. At the experimental conditions considered the technique of Fourier spectroscopy in combination with atomic emission analysis provides analytical calibration curves linear over about 3 orders of magnitude change in analyte concentration.
8. By comparison of the magnesium study reported in this chapter on which no smoothing operation has been applied and the magnesium study reported in Chapter 3 carried out with one level zero filling and Gaussian apodization, no appreciable difference in behavior is observed. The severe self apodization due to drive error is probably responsible for this observed behavior.

Finally, it is clear that calculation of complete standard deviation and signal-to-noise ratio spectra provides a powerful method for elucidating the noise characteristics and behavior of a spectrochemical measurement system and technique such as ICP-FTS.

CHAPTER 5

NOISE BEHAVIOR AND QUALITATIVE PERFORMANCE OF A FOURIER SPECTROMETER WITH AN INDUCTIVELY COUPLED PLASMA AS A SOURCE - PART II. EFFECT OF ADDING TO THE SOUGHT-FOR ELEMENT VARIOUS AMOUNTS OF A SECOND ELEMENT

I. Introduction

The study presented in this chapter deals with the effect of matrix elements on the noise behavior and characteristics of a low level sought-for element. Although this study is complementary to the one described and discussed in Chapter 4.III, it will be treated separately. The reason is that the noise characteristics, when the sought-for element is present with other elements, has a central role in the practical utilization of Fourier spectrometry in trace atomic emission analysis. The theory, in fact, predicts that the presence of elements other than the sought-for element, particularly at high levels, causes a deterioration of the limit of detection figure of the sought-for element.

II. Experimental Conditions

Three separate groups of solutions were prepared. Each group contained 10 ppm of magnesium (the designated sought-for element) and different amounts of the three elements, iron, manganese and zinc.

The first group contained 200 ppm, 400 ppm, 800 ppm, and 1600 ppm of iron; the second, 100 ppm, 200 ppm, and 400 ppm of manganese; and the third, 100 ppm, 200 ppm, and 400 ppm of zinc. The reason for choosing these three elements was to provide a variety of experimental conditions in which to test the noise behavior of sought-for element. In the ultraviolet spectral region iron has a complex spectrum with a large number of peaks, manganese has only three major peaks in the spectral region where the iron peaks appear, whereas zinc has three spectral peaks in a different spectral region.

Throughout the whole study the experimental conditions were kept exactly the same and they were the same as those described in Chapter 4.

III. Emission, Standard Deviation and Signal-to-Noise Ratio Spectra

As an example of the three groups of solutions only the spectra with the highest concentration of added matrix element are shown in the following figures.

The emission spectrum of a solution containing 10 ppm of magnesium and 1600 ppm of iron is displayed in Figure 41. The two major magnesium peaks at 279.6 nm and at 280.3 nm appear small whereas the two major iron peaks at 238.2 nm and at 259.9 nm have high intensity values. The spectral region which appears to the right of the two major magnesium peaks and contains essentially all the iron peaks has been expanded into two equal portions (Figure 42a-b). A total of 36 iron peaks belonging to two spectral alias regions have been successfully identified. They range from about 230 nm to about 270 nm and they are labelled by using the literature values. The observed values differ from the literature values by about ± 3 wavenumbers. For the spectral region considered this corresponds to an error ranging from 0.015 to 0.021 nm. The emission, standard deviation and signal-to-noise ratio spectra for the solution containing 10 ppm of magnesium and 1600 ppm of iron are displayed in Figure 43. The standard deviation spectrum, as usual suggests that the noise is mainly localized on peaks and the signal-to-noise ratio spectrum has the typical emission spectrum appearance.

Only three major manganese peaks appear in the emission spectrum of a solution containing 10 ppm of magnesium and 400 ppm of manganese (Figure 44): MnII

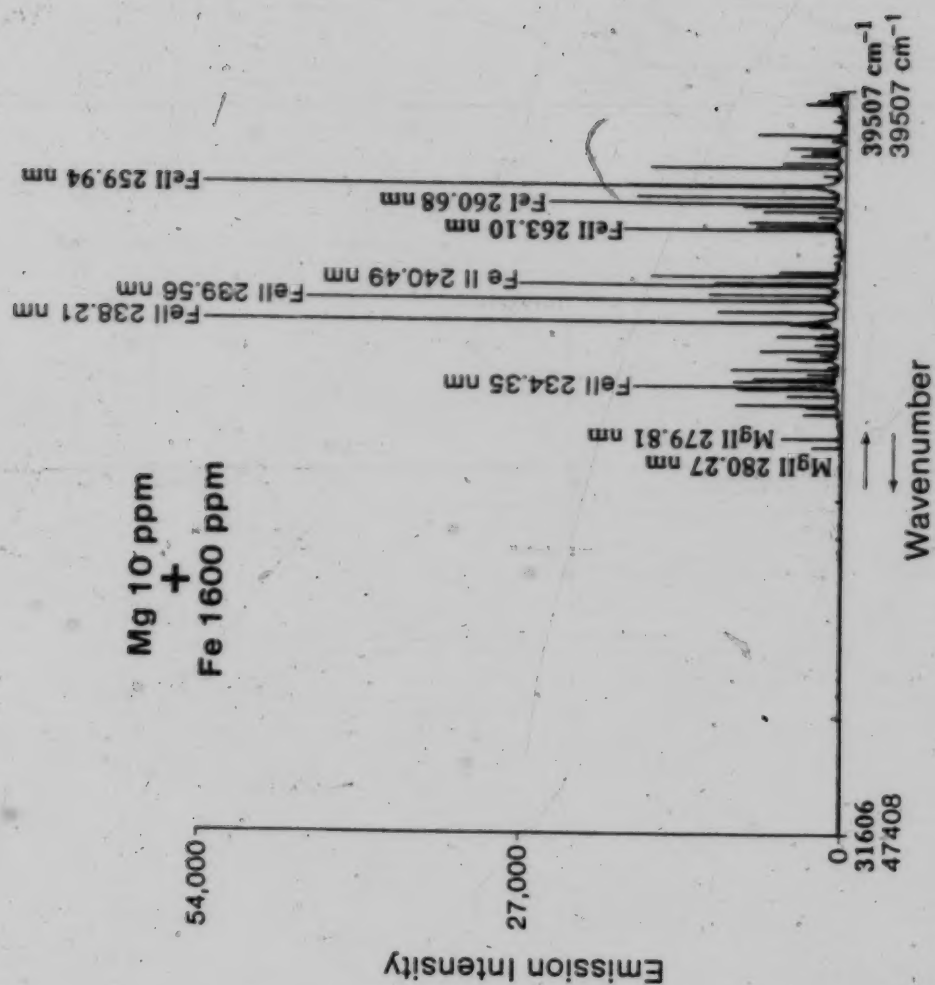


Figure 41. Emission spectrum of a solution containing 10 ppm of magnesium and 1600 ppm of iron in the ultraviolet spectral region.

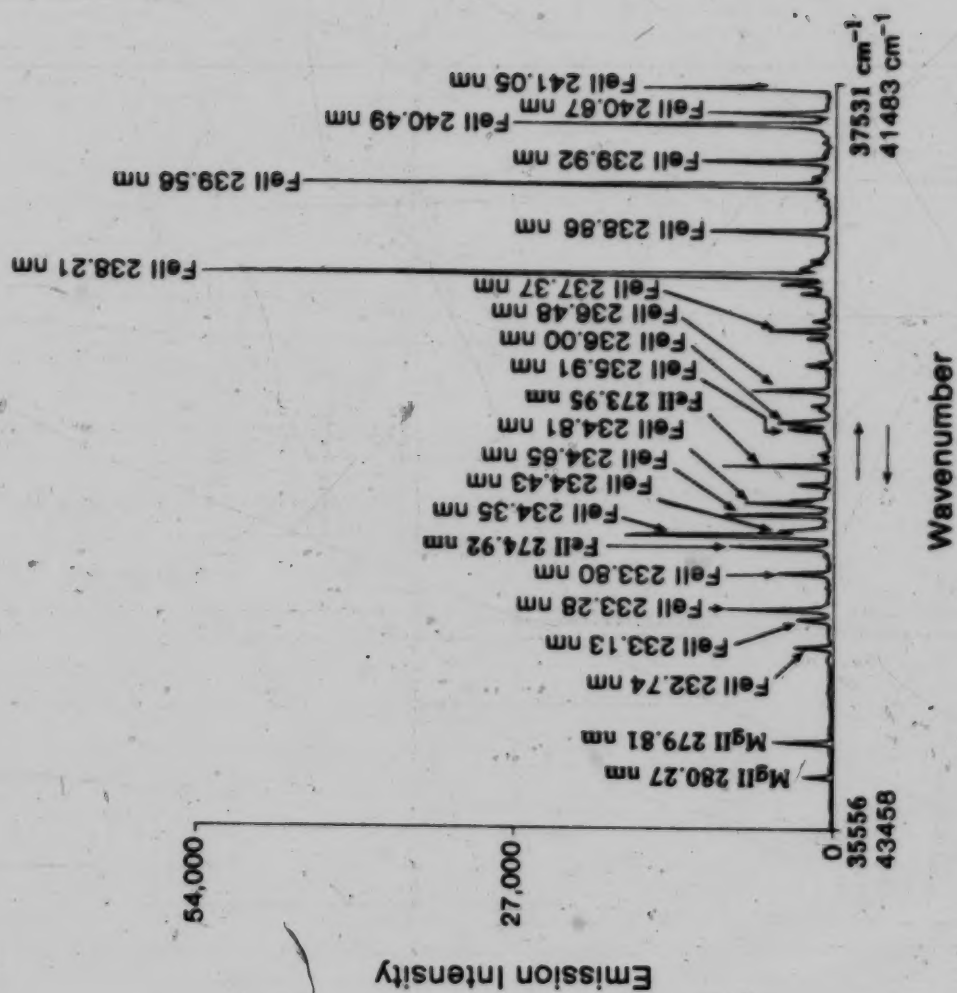


Figure 42. (a) Emission spectrum of a solution containing 10 ppm of magnesium and 1600 ppm of iron in the ultraviolet spectral region, part 1.

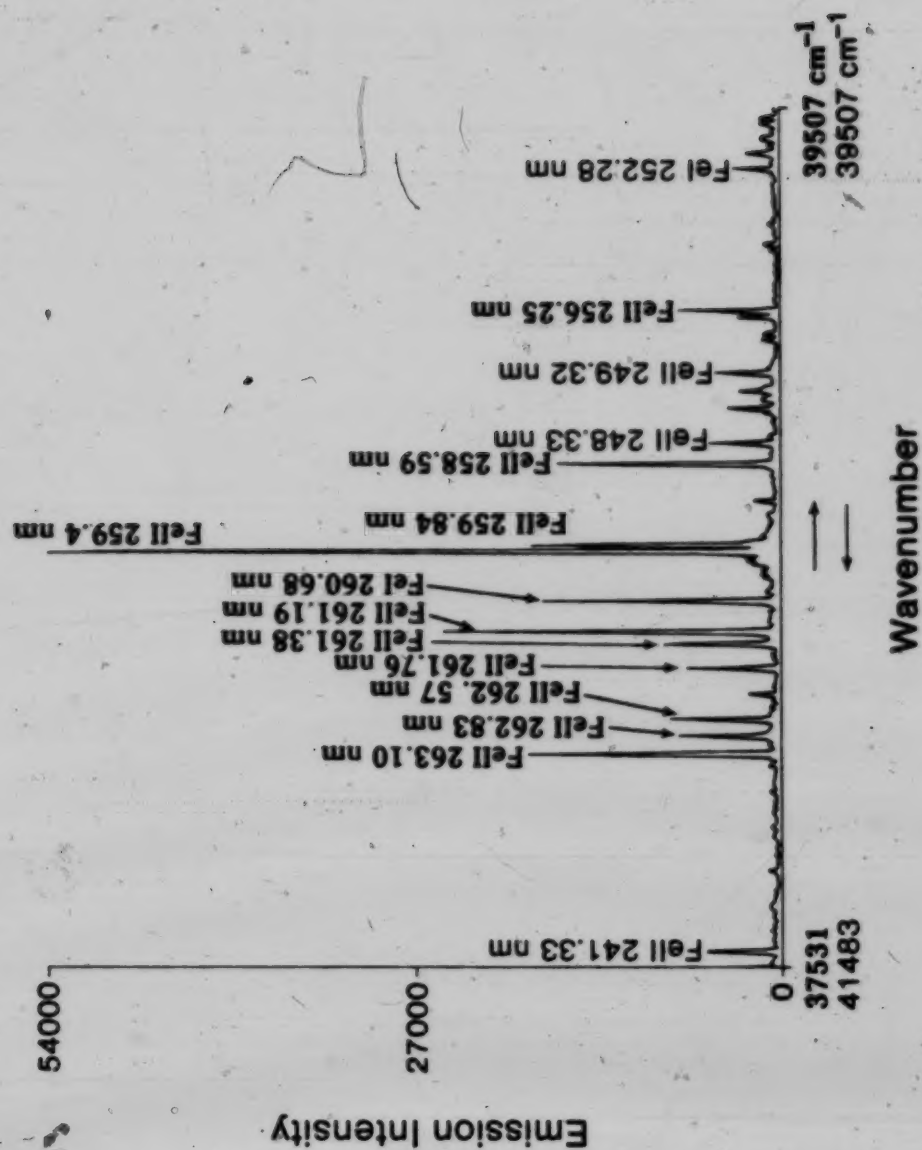
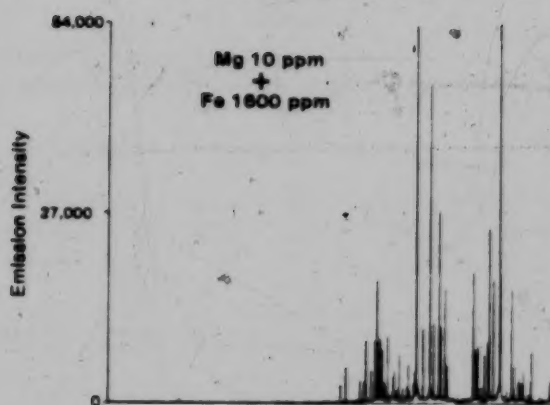


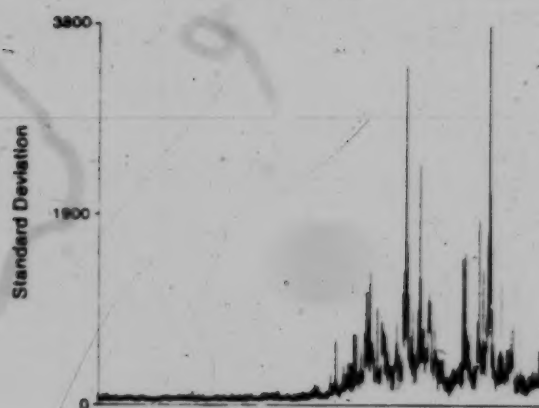
Figure 42. (b) Emission spectrum of a solution containing 10 ppm of magnesium and 1600 ppm of iron in the ultraviolet spectral region, part 2.

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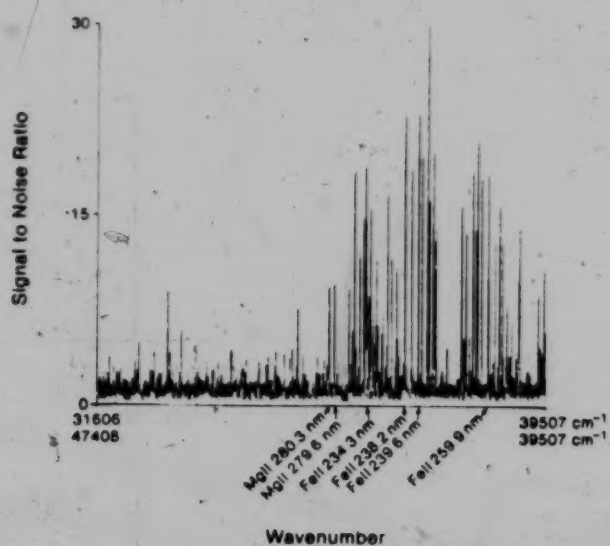
Emission Spectrum



STD. DEV. Spectrum



S.N.R. Spectrum



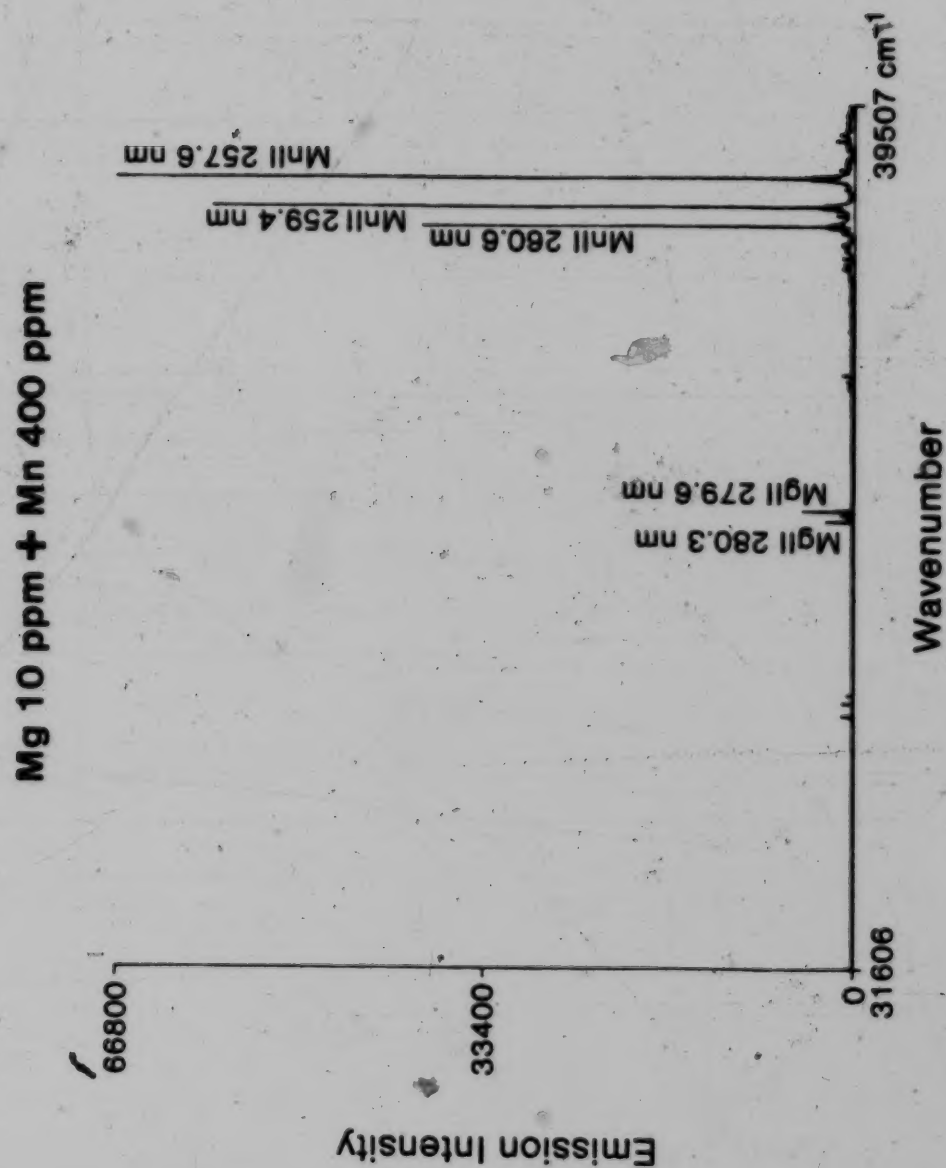


Figure 44. Emission spectrum of a solution containing 10 ppm of magnesium and 400 ppm of manganese in the ultraviolet spectral region.

257.6 nm, MnII 259.4 nm, and MnII 260.6 nm. In a scale expanded ($\times 32$) emission spectrum (Figure 45) fourteen more peaks have been identified. They include the ionic triplet at about 294 nm and the ionic quintuplet at about 270 nm. The emission standard deviation and signal-to-noise ratio spectra for this solution are shown in Figure 46.

A solution containing 10 ppm of magnesium and 400 ppm of zinc gives the emission spectrum shown in Figure 47. The three major zinc peaks appear at the left of the magnesium peaks and are affected by very pronounced spurious spectral features. The corresponding emission, standard deviation and signal-to-noise ratio spectra are shown in Figure 48.

The spectral noise behavior observed will be treated under the three following headings: (IV) noise behavior of the added element, (V) noise behavior of the background, and (VI) noise behavior of the sought-for element.

IV. Noise Behavior of the Added Element

The peak area emission intensities relative to the peaks of the element added were calculated according to the procedure outlined in Chapter 4. The average values of the peak areas of the two major peaks of the

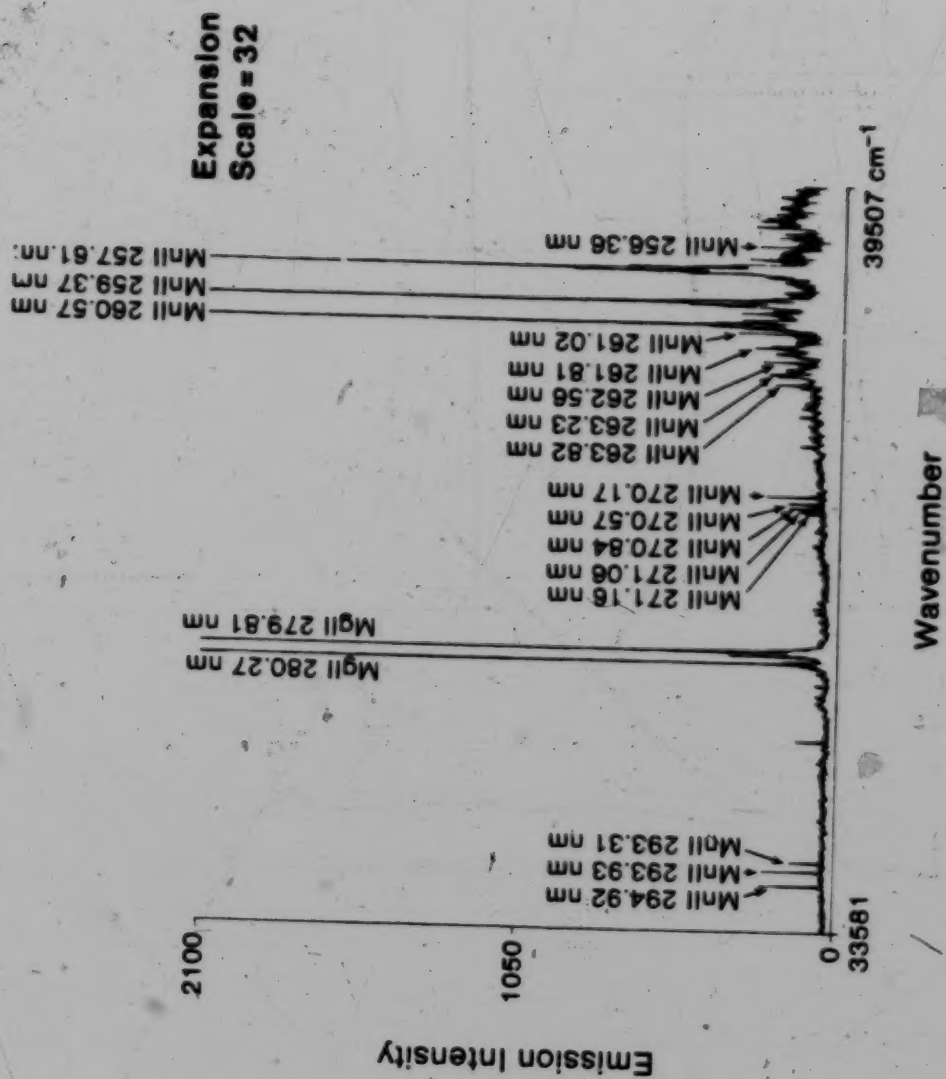
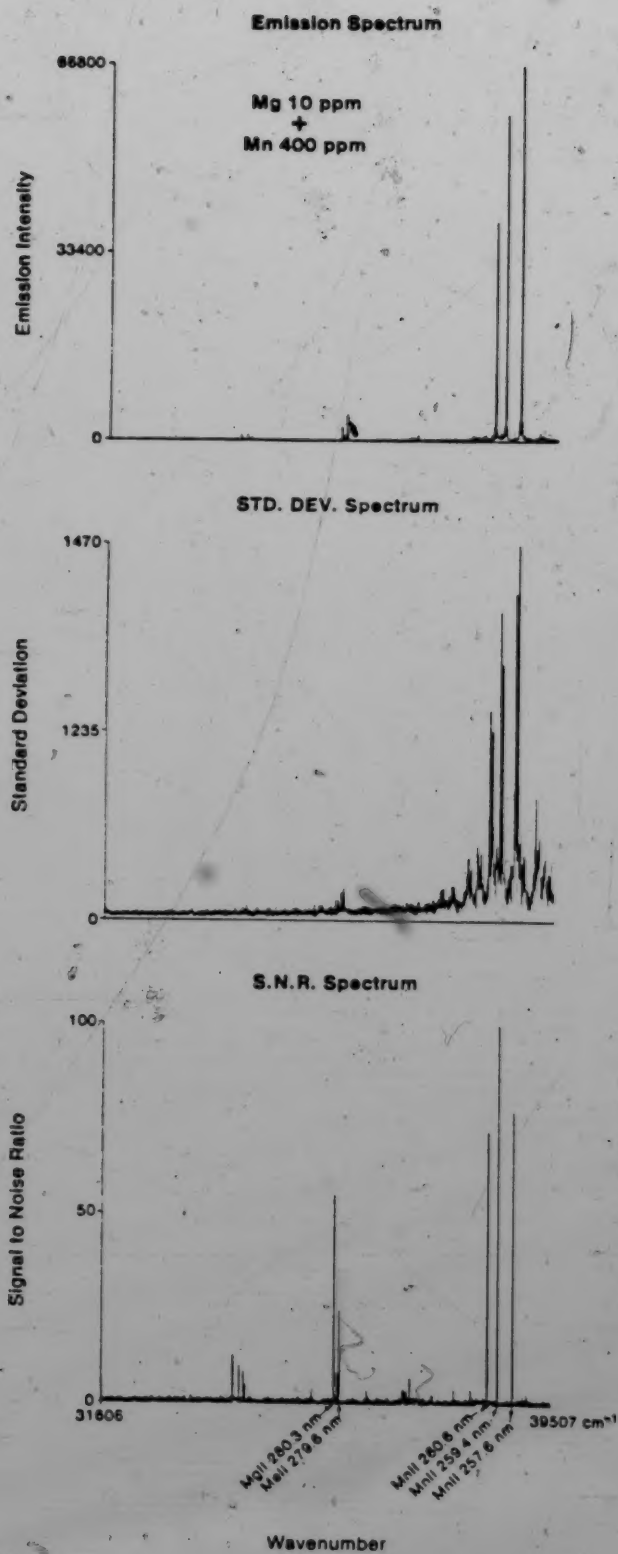


Figure 45. Partial emission spectrum of a solution containing 10 ppm of magnesium and 400 ppm of manganese in the ultraviolet spectral region.



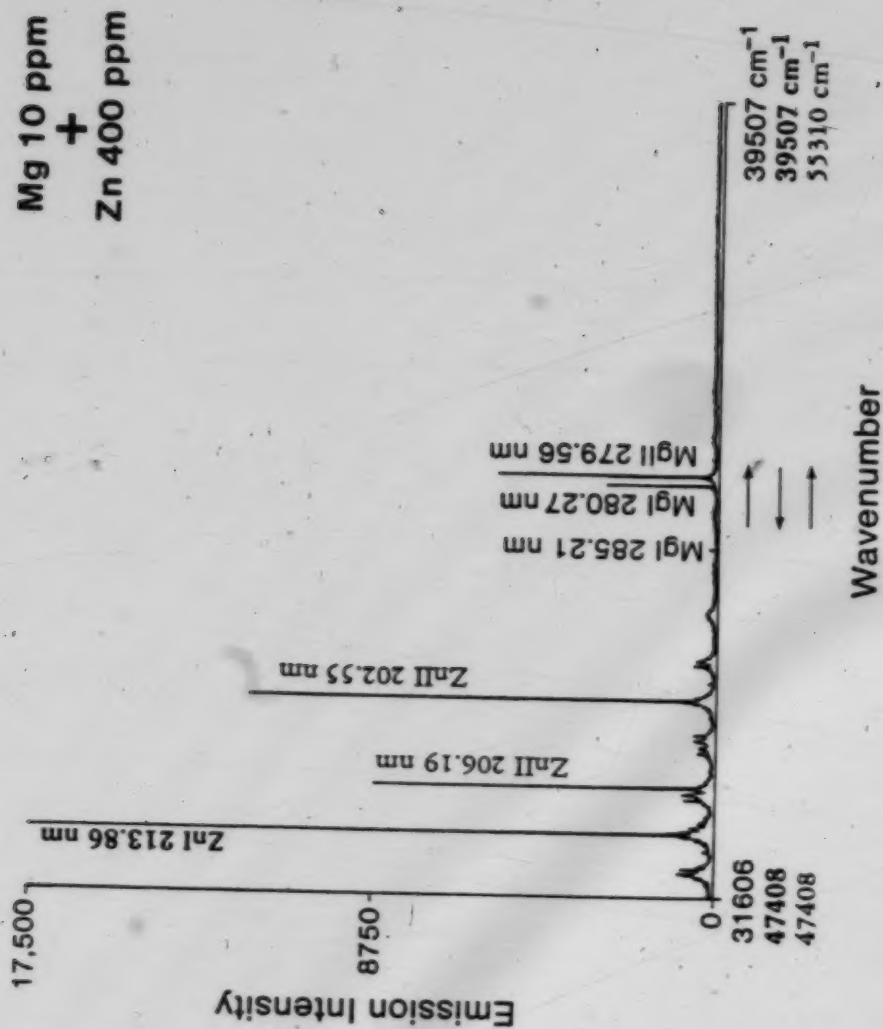
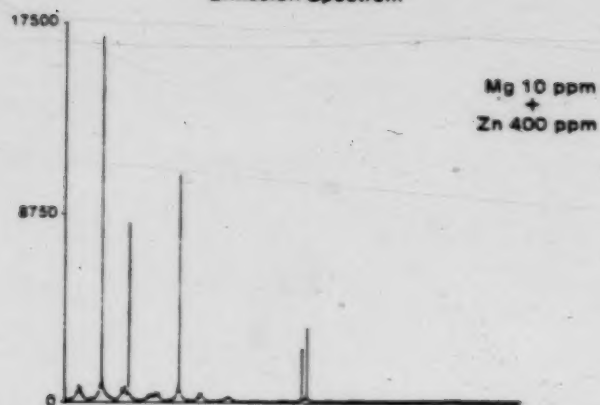


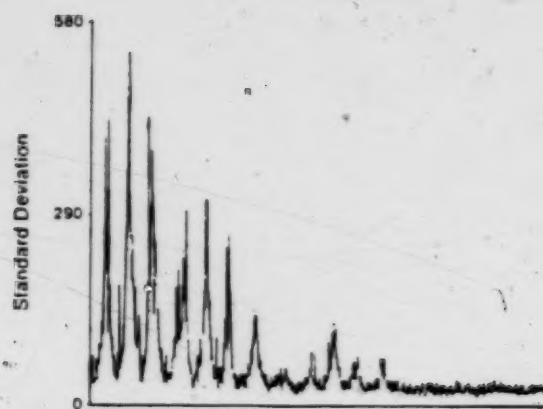
Figure 47. Emission spectrum of a solution containing 10 ppm of magnesium and 400 ppm of zinc in the ultraviolet spectral region.

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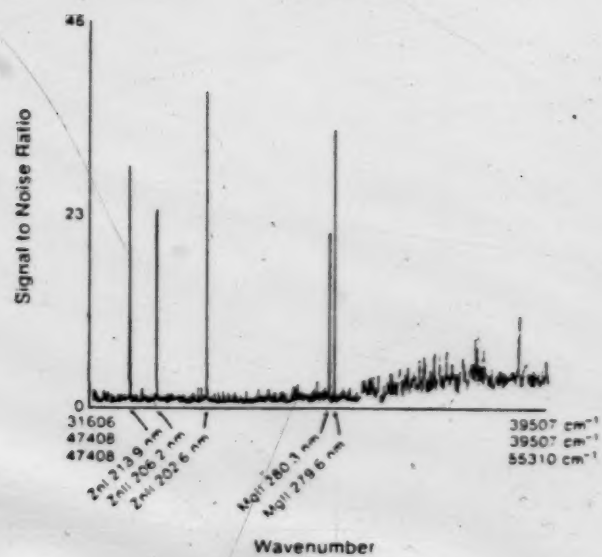
Emission Spectrum



STD. DEV. Spectrum



S.N.R. Spectrum



element added as a function of the concentration of element added (analytical calibration curves) are reported at the top of Figure 49. The corresponding standard deviation values as a function of the concentration of element added are given in the middle portion of the same figure.

The analytical calibration curve for manganese is linear with a slope of 0.99; for iron it is linear for the first three concentrations (slope = 1.02) and curves towards the axis of the abscissa for the solution containing 1600 ppm of iron. The zinc calibration curve on the other hand is of poor quality. This poor analytical performance for zinc may, in part, be due to the short wavelengths of the Zn lines. This difference in wavelength can result in a substantial phase difference in the experimentally acquired interferogram. This fact is apparent from an observation of Figures 50 and 51 where the double sided interferograms for a solution of 10 ppm of magnesium and for a solution of 100 ppm Zn and 10 ppm Mg are shown. The latter exhibits an asymmetrical shape whereas the first is symmetrical about the 2049 point or zero path difference point. The same symmetrical shape is likewise obtained for a double sided interferogram of a solution of 10 ppm of magnesium added to 100 ppm of iron (Figure 52). The asymmetrical shape of the interferogram

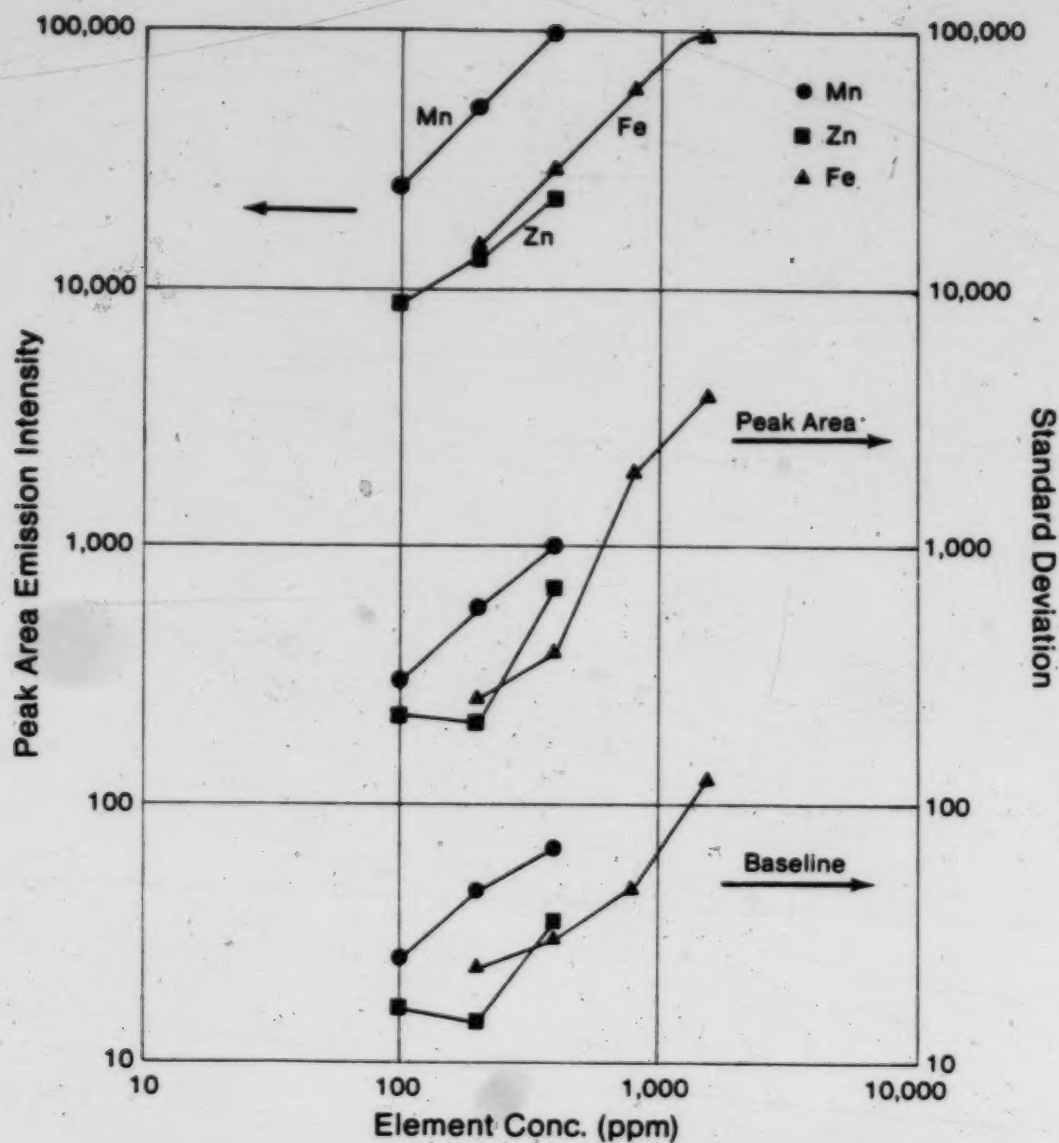


Figure 49. Plots of peak area and standard deviation emission intensity of the two major peaks of the elements added, and baseline standard deviation as a function of the concentration of the element added.

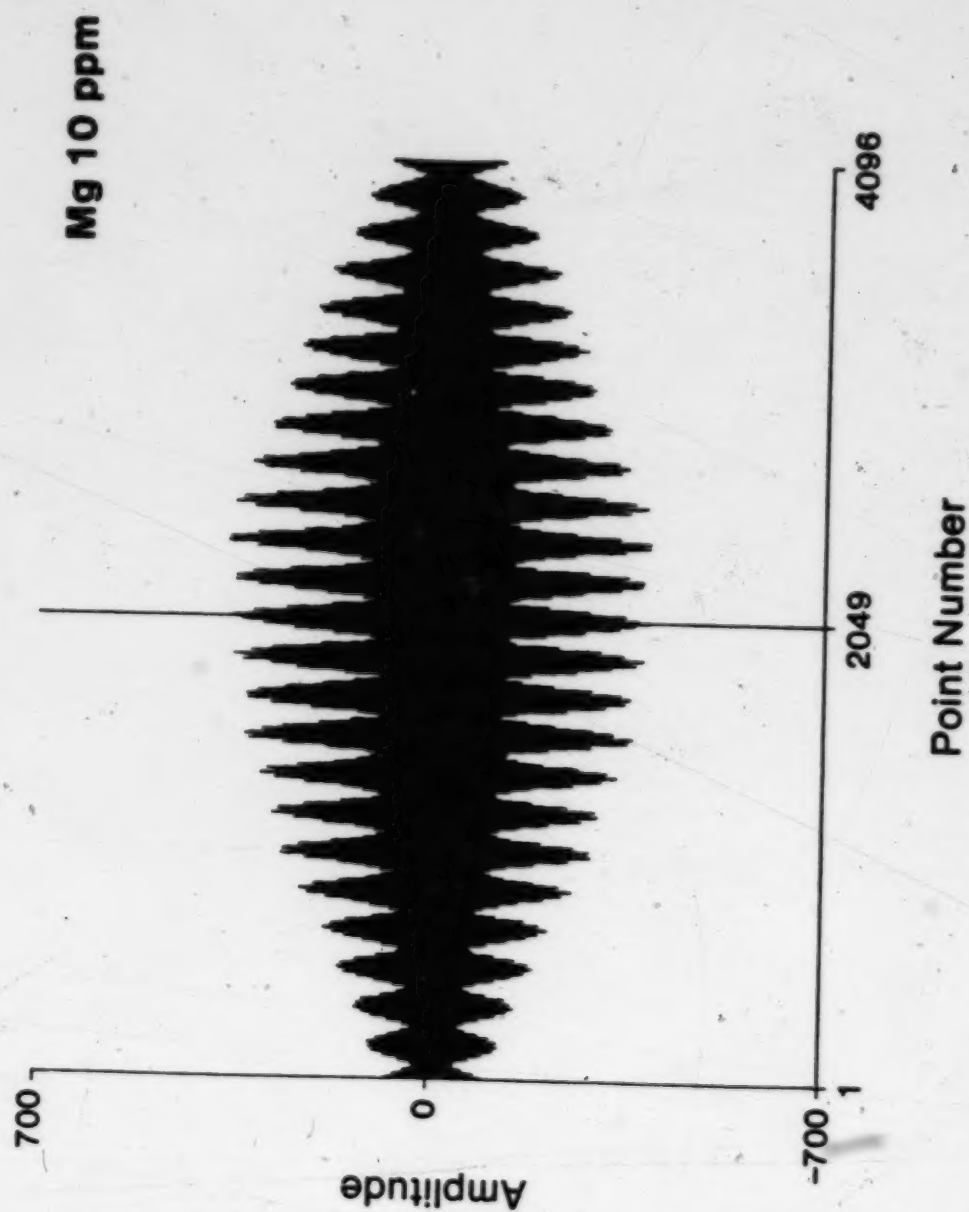


Figure 50. Double sided amplitude interferogram of a solution containing 10 ppm of magnesium.

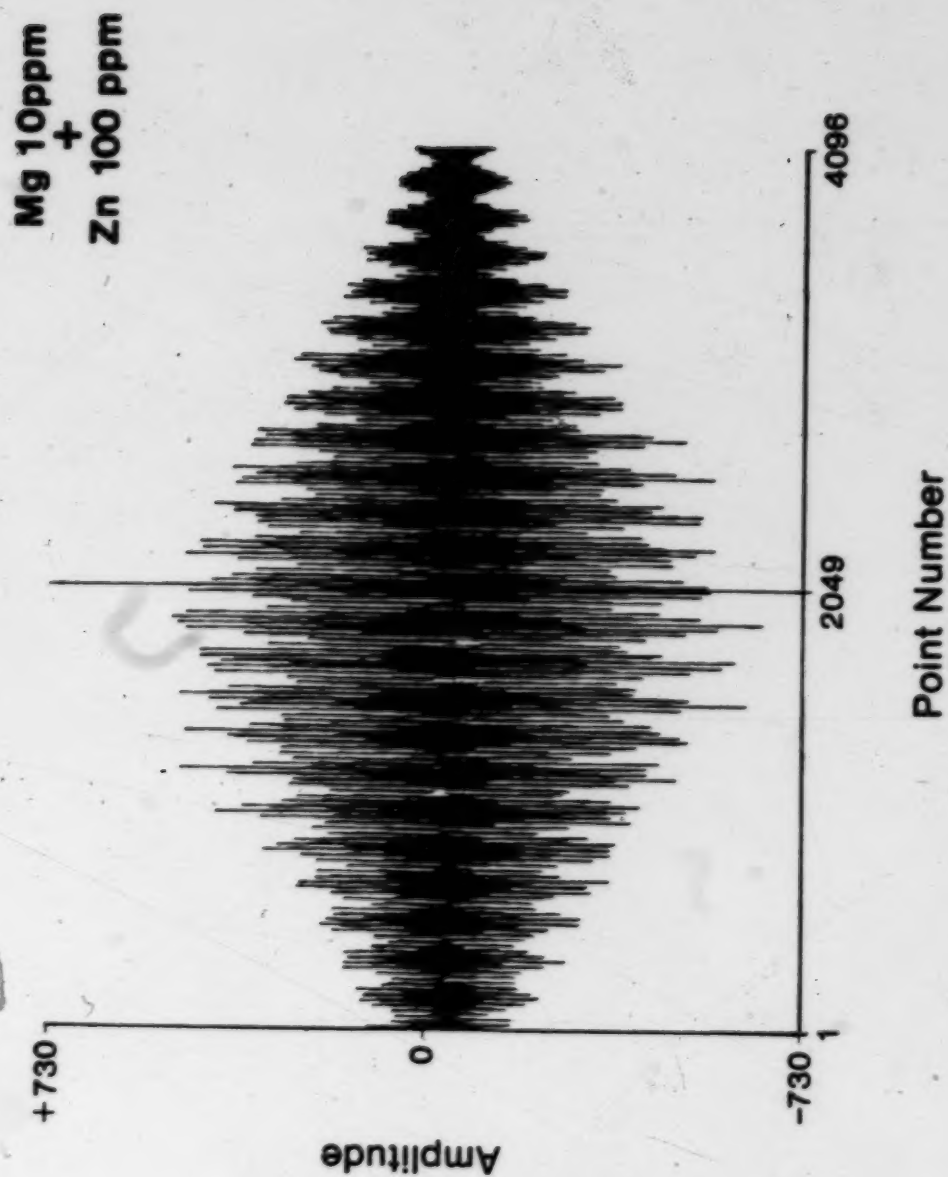


Figure 51. Double sided amplitude interferogram of a solution containing 10 ppm of magnesium and 100 ppm of zinc.

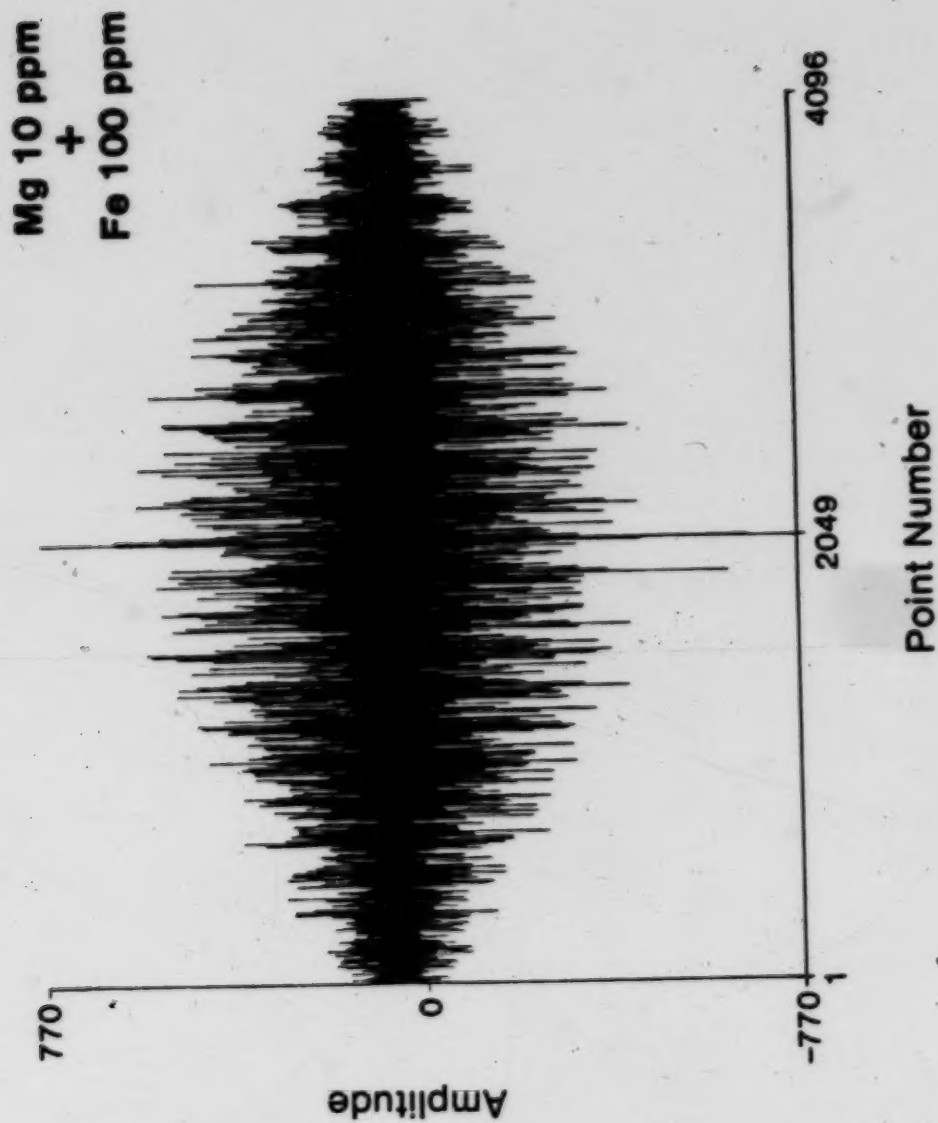


Figure 52. Double sided amplitude interferogram of a solution containing 10 ppm of magnesium and 100 ppm of iron.

makes the monitoring of the reproducibility of experimental conditions a very arduous task to perform. Moreover, the fact that the wavelengths of zinc are very short renders the acceptable error for obtaining reproducible results small and increases the difficulty in maintaining the experimental conditions stable.

Finally (with reference to Figure 49), as the peak area standard deviation behavior indicates, an increase of the noise is paralleled by an increase of the concentration of the element added, although the zinc peak area standard deviation has an anomalous behavior: it decreases as the concentration of zinc increases from 200 to 400 ppm.

V. Noise Behavior of the Background

The background standard deviation as a function of the concentration of the element added is shown at the bottom of Figure 49. The background standard deviation reported is the average between the values in two different spectral regions. In each spectral region (spectral points 100 to 115 and 1600 to 1615) 8 points have been chosen to calculate the standard deviation. The background standard deviation increases as the concentration of the element added increases. Its behavior parallels the peak area standard deviation

behavior even if it is much lower in absolute value. This fact contradicts strongly the theory that predicts equal noise distribution along the spectral axis.

The calculation of the rate of change of the peak and background standard deviation values is impractical due to limited number of points available. Nevertheless the fact that the background standard deviation increases when the concentration of element added is increased is a clear indication that to some degree the multiplex disadvantage is a reality. The fact that the background standard deviation is dependent upon its distance from the spectral region containing the peaks is shown in Figure 53, where the background standard deviations for the two regions are plotted separately. The background standard deviation value in the spectral range included between point #1600 and 1615 is higher for solutions containing peaks closer to this spectral range (iron and manganese) whereas its value in the spectral range included between points 100 and 115 is higher for the solution containing zinc.

VI. Noise at Peaks of Sought-for Element

The effect of adding a high concentration of a second element on the noise behavior of the sought-for element is graphically represented in Figure 54. The signal-to-noise ratio spectra in the region

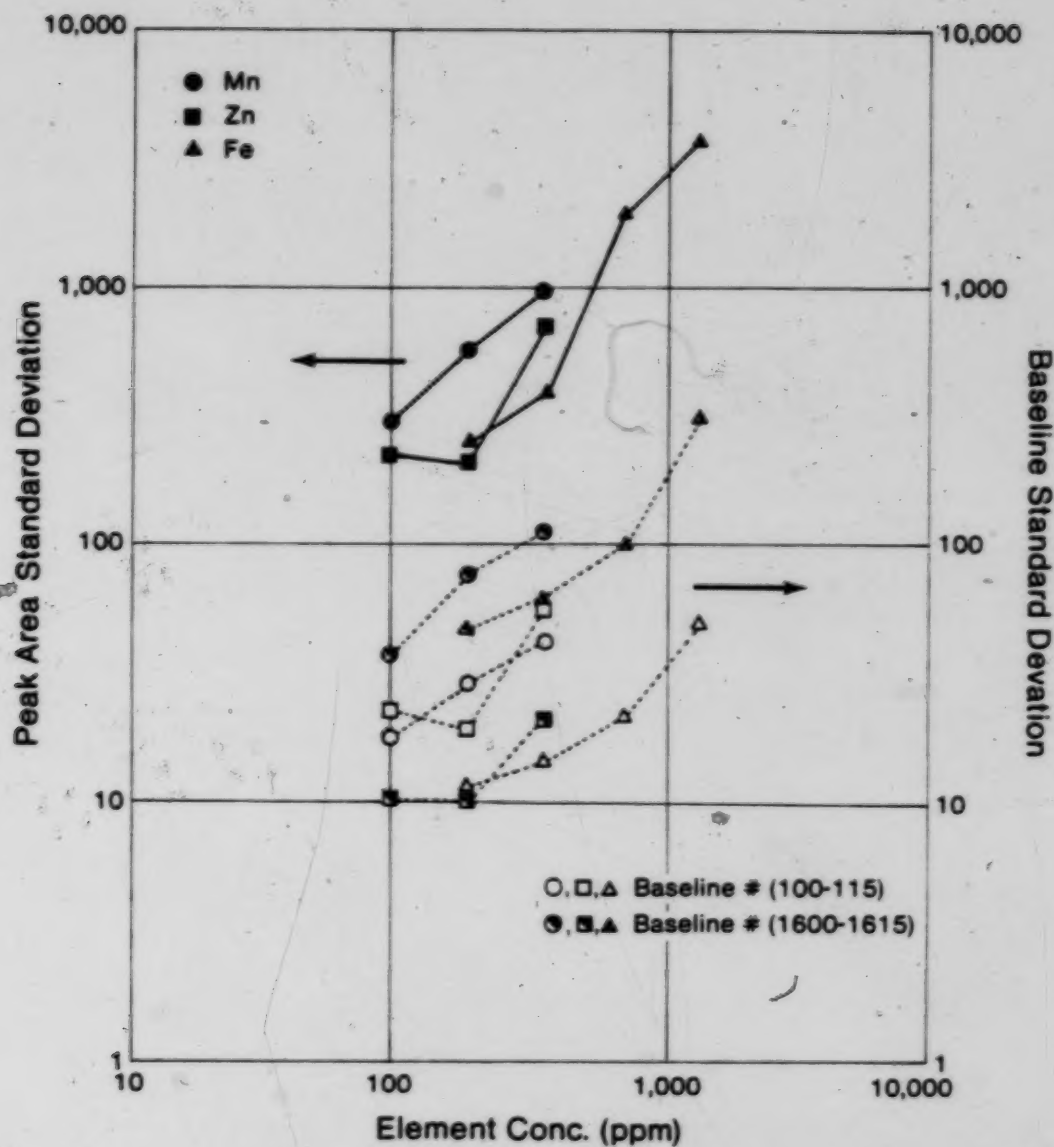
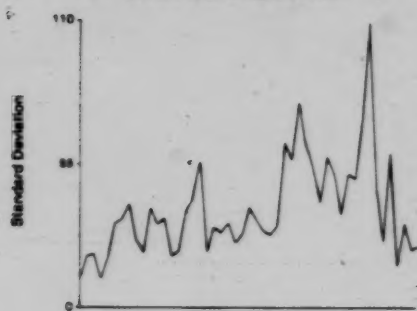


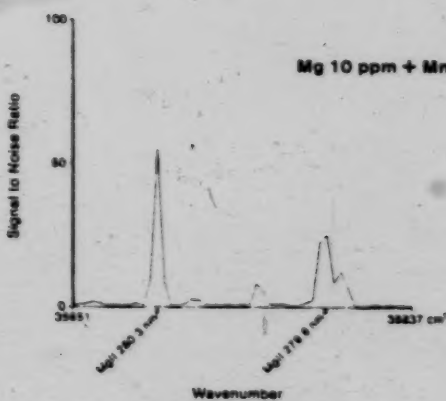
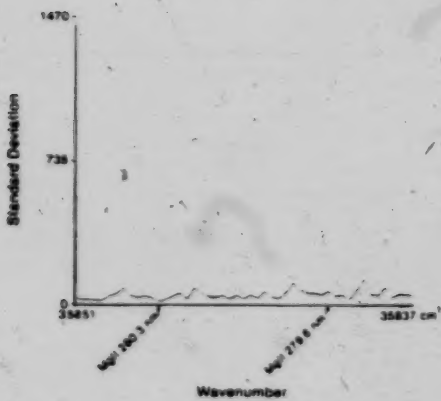
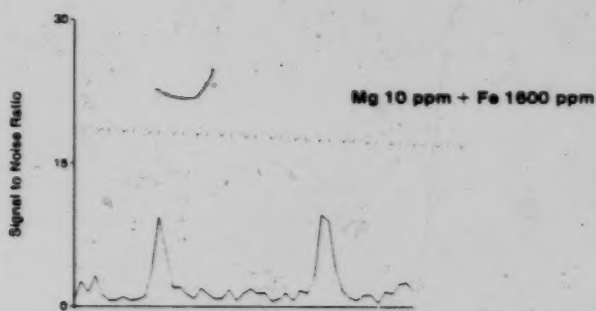
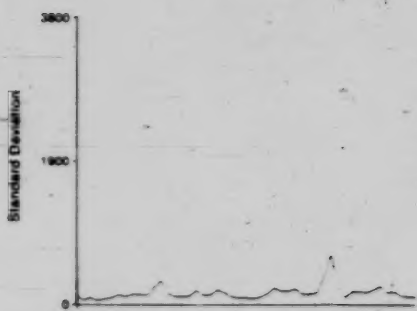
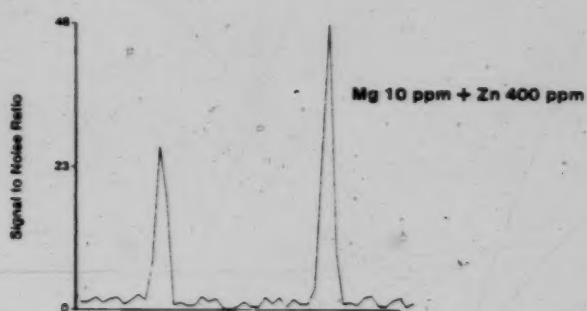
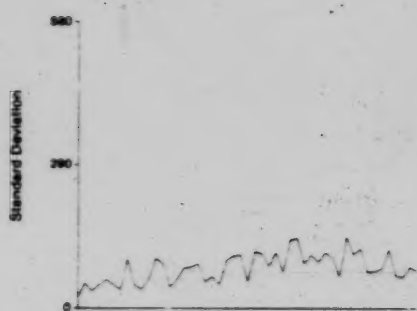
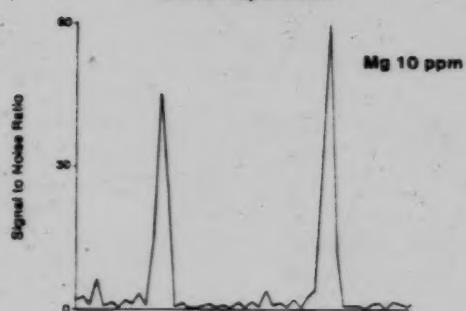
Figure 53. Plots of peak area standard deviations of the two major peaks of the element added and baseline standard deviation as a function of the concentration of the element added.

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STD. DEV. Spectrum



S.N.R. Spectrum



around the two major magnesium peaks of solutions containing 10 ppm of magnesium, 10 ppm of magnesium and 400 ppm of zinc, 10 ppm of magnesium and 1600 ppm of iron, and 10 ppm of magnesium and 400 ppm of manganese are shown in this figure.

The consequences of adding a large amount of a matrix element (or increasing considerably the power signal hitting the detector) are:

1. a general decrease of the signal-to-noise ratio at the analyte peaks.
2. a general decrease in peak localization of the noise is noticed even if the actual value is increased.
3. In the case of the addition of 1600 ppm of Fe the loss of the magnesium peak precision is the same for both peaks; in the case of the addition of 400 ppm of Mn, the loss in precision, even if more limited than in the previous case, is higher for the MgII 279.6 nm peak than the MgII 280.3 nm peak. The closeness of the MgII 279.6 nm peak to the MnI 279.5 can be responsible for this behavior.
4. Zn appears to have the least effect.

The plot of peak area signal-to-noise ratio for the MgII 279.6 nm peak as a function of the concentration of element added is shown in Figure 55. The value of the peak area signal-to-noise ratio for the solution

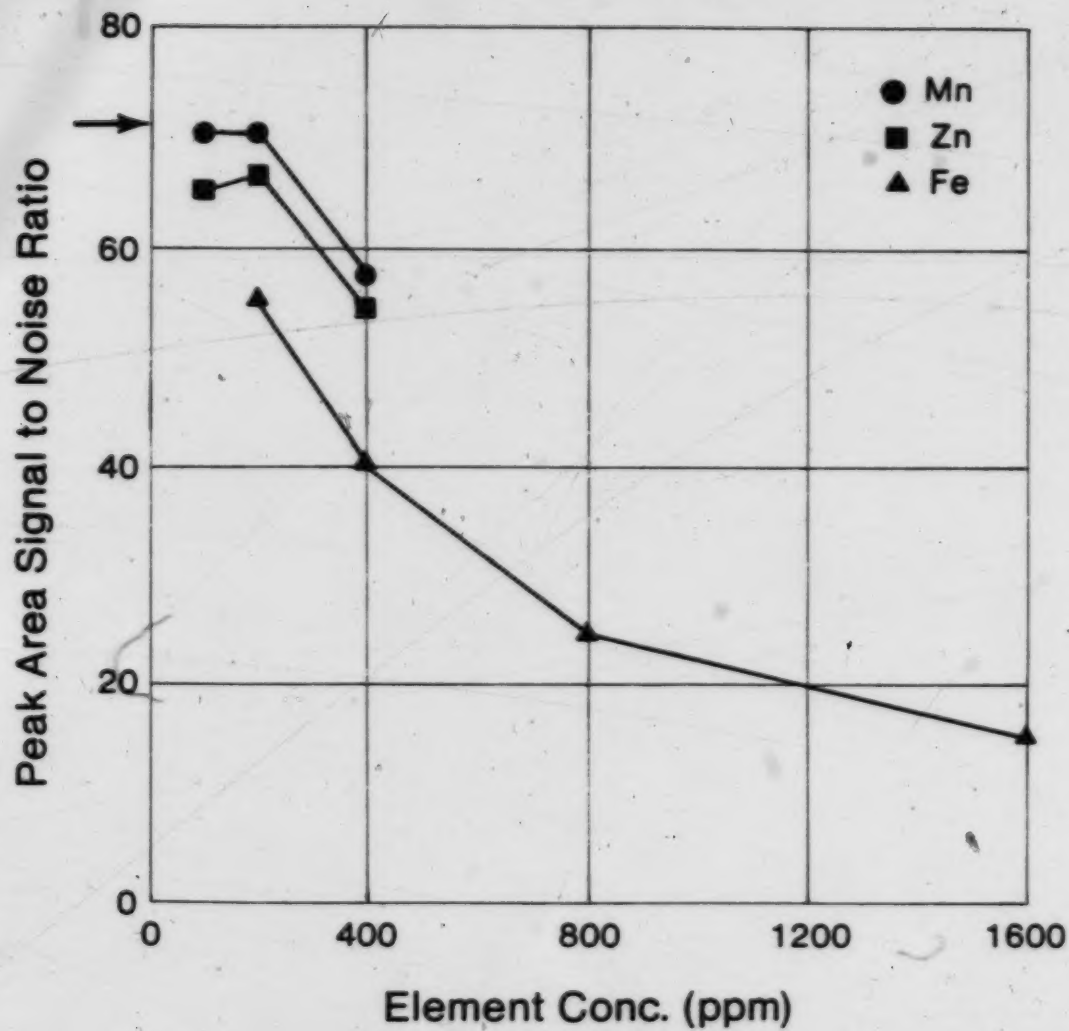


Figure 55. Plots of peak area signal-to-noise ratio for the MgII 279.6 nm peak as a function of the element added.

containing only 10 ppm of magnesium is indicated by the arrow. This figure suggests a definite trend of decrease in signal precision of the sought-for element as an increasing amount of a second element is added.

This signal precision deterioration is higher the higher the concentration of the element added and the larger the number of peaks this element adds to the original spectrum. No effect is felt on the sought for analyte signal up to 200 ppm of manganese added but a high degradation in signal quality is obtained after addition of 1600 ppm of iron.

VII. Limit of Detection in Fourier Spectroscopy

The limit of detection (LOD) is obtained by calculating the concentration that corresponds to three times the standard deviation of the background. The procedure is fairly straightforward in conventional dispersive spectroscopy as the background standard deviation is not normally highly matrix dependent. It is clear that this is not the case in Fourier spectroscopy where the background standard deviation is a function of the total amount of light hitting the detector. The limit of detection of the analyte considered is therefore dependent upon how many elements are present in excess of the analyte itself, their concentrations and how many

peaks they add to the total signal, in other words is dependent upon the types of sample, i.e. in FTS the limit of detection is sample dependent. By consequence it is virtually impossible to report a unique value of the limit of detection for the analyte considered that is valid for all experimental conditions. In Table 8 the calculated limits of detection of magnesium in all the solutions considered in this study reported in this chapter are given. They were calculated considering the analyte signal for the peak area of the MgII 279.6 nm peak and are reported for the two different background spectral regions considered.

In order to avoid including supplementary noise caused by peak localization, the baseline region far removed from the peaks of the added element is considered. In this case the increase in LOD value is a measure of the multiplex disadvantage. Also the RMS of the interferogram represents the total signal power hitting the detector (refer to Chapter 4). By comparing the increase in LOD with the calculated RMS we can obtain information on how the multiplex disadvantage increases as a function of the total signal.

The calculated LOD and RMS interferogram values are tabulated together and are presented in Table 9. If we consider only the largest amount of element added with

Table 8
Limits of Detection of Magnesium in Various Solutions

Solution Containing	LOD (100-115) ppb	LOD (1600-1615) ppb
10 ppm Mg	23	18
10 ppm Mg + 200 ppm Fe	48	191
10 ppm Mg + 400 ppm Fe	52	244
10 ppm Mg + 800 ppm Fe	84	400
10 ppm Mg + 1600 ppm Fe	204	1200
10 ppm Mg + 100 ppm Mn	60	148
10 ppm Mg + 200 ppm Mn	119	319
10 ppm Mg + 400 ppm Mn	168	450
10 ppm Mg + 100 ppm Zn	91	42
10 ppm Mg + 200 ppm Zn	70	40
10 ppm Mg + 400 ppm Zn	232	83

Table 9
Limits of Detection of Magnesium and RMS Values
in Various Solutions

Solution Containing	LOD (100-115) ppb	LOD (1600-1615) ppb	RMS Interferogram
10 ppm Mg	23	18	11
+ 200 ppm Fe	48	-	30
+ 400 ppm Fe	52	-	54
+ 800 ppm Fe	84	-	80
+ 1600 ppm Fe	204	-	113
10 ppm Mg			
+ 100 ppm Mn	60	-	28
+ 200 ppm Mn	119	-	52
+ 400 ppm Mn	168	-	95
10 ppm Mg			
+ 100 ppm Zn	-	42	16
+ 200 ppm Zn	-	40	26
+ 400 ppm Zn	-	83	46

respect to no element added, in case of the addition of:
(a) 1600 ppm of Fe the LOD increases 8.9 fold for a 10.3 RMS value increase; (b) 400 ppm of Mn the LOD increases 7.3 fold for a 8.6 RMS value increase; and (c) 400 ppm of Zn the LOD increases 4.6 fold for a 4.2 RMS value increase. With the exception of the zinc case, which may be anomalous, the increase in LOD is about 0.85 of the increase of the RMS values. This indicates an almost linear relationship between the extent of the deterioration of the limit of detection and the total signal increase.

VIII. Conclusions

The same characteristics of spectral noise localization observed in the data reported in Chapters 3 and 4 are noticeable in the data described in this chapter. The operation of adding another element affects the analyte element quantitative performance. A substantial signal-to-noise ratio decrease in the analyte signal is noticed, particularly in the case when large amounts of iron, which contributes a great number of peaks, was added to the analyte.

The second effect is the increase of the calculated limit of detection of analyte. This characteristic, which can be assimilated to a multiplex disadvantage effect, is highly undesirable in trace elemental analysis.

A quasi-linear relationship exists between the increase of the multiplex disadvantage effect and the total signal as represented by the RMS of interferogram. A twenty-fold increase in the analyte limit of detection is experimentally observed in the case of 1600 ppm of added iron.

CHAPTER 6

SUMMARY AND FUTURE RESEARCH DIRECTIONS

In conclusion, noise studies have been carried out to assess the feasibility of ICP-FTS for elemental analysis. Analyte calibration curves linear over three orders of magnitude were obtained and the precision ranged between 1 and 2% R.S.D.

Statistical data along the calibration plots were measured and calculated in order to identify the nature of the limiting noise at various analyte concentration ranges. The sample dependent limit of detection, which can be considered a "weak" prerogative of ICP-FTS in the analysis of elements present in traces, did not seem to create unmanageable problems.

All these results are encouraging and seem to indicate that the ICP-FTS has a great potential to become a viable technique for elemental analysis. Moreover, a noise study such as the one described in this thesis can be considered a viable means for the analysis of the technique. These noise studies lead to the identification of noise and errors of spurious nature present at the experimental conditions.

Along the way the importance of standard deviation

and signal-to-noise ratio spectra in giving a complete picture of the noise behavior of the experimental procedure became clear.

The improvement of the quality of the mirror drive mechanism and the overall stability of the spectrometer system have to be considered research directions which deserve priority attention. They should entail: (a) the construction of a thermally controlled enclosure for the spectrometer, (b) the development of a better drive system, and (c) the construction of devices and the conception of methods to compensate for optical misalignment, loss of parallelism of the mirror movement and drift.

The development of a new mirror drive system based on two opposing magnetic load coils and a square air bearing along with the investigation of methods such as the use of piezoelectrical devices and electronic feedback loops to ensure real time compensation for optical misalignment is currently underway in our laboratory [114].

Other research directions that require attention are:

1. Investigation of parameters and standards that can be used to optimize experimental conditions (RMS values, major peak emission intensity, etc.).
2. Investigation of means of compensating for source fluctuation at the level of the interferogram signal

(internal modulation, interferograms, ratio, etc.).

In conclusion the ICP-FTS has all the attributes to become a viable technique for elemental analysis and research if an ICP-FTS spectrometer that eliminates the complication due to aliasing and allows high resolution performance can be built.

Research in both directions which involve the use of fast data collection and processing rates are underway in our laboratory [115].

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